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World Health Organization

Pesticide residues in food 1999

Joint FAO/WHO Meeting on Pesticide Residues

EVALUATIONS

1999

PART I - RESIDUES

Rome, 2000

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* First evaluation
** Evaluation in CCPR periodic review programme

1999 JOINT MEETING OF THE FAO PANEL OF EXPERTS ON PESTICIDE RESIDUES IN FOOD AND THE ENVIRONMENT AND THE WHO CORE ASSESSMENT GROUP

Rome, 20-29 September 1999

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ABBREVIATIONS WHICH MAY BE USED

(Well-known abbreviations in general use are not included)

Ache	acetylcholinesterase
acute RfD	acute reference dose
ADI	acceptable daily intake
AFI(D)	alkali flame-ionization (detector)
ai	active ingredient
ALAT	alanine aminotransferase
AR	applied radioactivity
ASAT	aspartate aminotransferase
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
bw	body weight
BOD	biological oxygen demand
CA	Chemical Abstracts
CAS	Chemical Abstracts Services
CCN	Codex Classification Number (this may refer to classification number for compounds or for commodities)
CCPR	Codex Committee on Pesticide Residues
CCRVDF	Codex Committee on Residue of Veterinary Drugs in Food
ChE	cholinesterase
CI	chemical ionization
CNS	central nervous system
cv	coefficient of variation
CXL	Codex Maximum Residue Limit (Codex MRL). See MRL.
DFG	Deutsche Forschungsgemeinschaft
DL	racemic (optical configuration, a mixture of dextro- and laevo-)
DP	dustable powder
DS	powder for dry seed treatment
DT-50	time for 50% decomposition (i.e. half-life)
DT-90	time for 90% decomposition
EBDC	ethylenebis(dithiocarbamate)
EC	(1) emulsifiable concentrate (2) electron-capture [chromatographic detector]
ECD	electron-capture detector
EI	electron-impact
EMDI	estimated maximum daily intake
EPA	Environmental Protection Agency
ERL	extraneous residue limit
ETU	ethylenethiourea
F_1	filial generation, first
F_2	filial generation, second
f.p.	freezing point

FAO	Food and Agriculture Organization of the United Nations
FDA	Food and Drug Administration
FI(D)	flame-ionization (detector)
FP(D)	flame-photometric (detector)
g (not gm)	gram
μg	microgram
GAP	good agricultural practice(s)
GC-MS	gas chromatography - mass spectrometry
GC-MSD	gas chromatography with mass-selective detection
G.I.	gastrointestinal
GL	guideline level
GLC	gas-liquid chromatography
GLP	good laboratory practice
GPC	gel-permeation chromatograph or chromatography
GSH	glutathione
h (not hr)	hour(s)
ha	hectare
Hb	haemoglobin
hl	hectolitre
HPLC	high-performance liquid chromatography
HPLC-MS	high-performance liquid chromatography - mass spectrometry
HR	highest residue in the edible portion of a commodity found in the trials .... used to estimate a maximum residue level in the commodity
HR-P	residue in a processed commodity calculated by multiplying the HR of .... the raw agricultural commodity by the corresponding processing factor
i.d.	internal diameter
IEDI	international estimated daily intake
IESTI	international estimate of short-term intake
i.m.	intramuscular
i.p.	intraperitoneal
IPCS	International Programme on Chemical Safety
IR	infrared
IRDC	International Research and Development Corporation (Mattawan, Michigan, USA)
i.v.	intravenous
JMPR	Joint FAO/WHO Meeting on Pesticide Residues (Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group
LC	liquid chromatography
LC_{50}	lethal concentration, 50%
LC-MS	liquid chromatography - mass spectrometry
LD_{50}	lethal dose, median
LOAEL	lowest observed adverse effect level
LOD	limit of determination (see also "*" at the end of the Table)
LSC	liquid scintillation counting or counter
M	molar
μm	micrometre (micron)
MFO	mixed function oxidase

min (no stop)	minute(s)
MLD	minimum lethal dose
mo (not mth.)	month(s)
MRL	Maximum Residue Limit. MRLs include draft MRLs and Codex MRLs (CXLs). The MRLs recommended by the JMPR on the basis of its estimates of maximum residue levels enter the Codex procedure as draft MRLs. They become Codex MRLs when they have passed through the procedure and have been adopted by the Codex Alimentarius Commission.
MS	mass spectrometry
MSD	mass-selective detection or detector
MTD	maximum tolerated dose
n (not *n*)	normal (defining isomeric configuration)
NCI	National Cancer Institute (USA)
NMR	nuclear magnetic resonance
NOAEL	no-observed-adverse-effect level
NOEL	no-observed-effect level
NP(D)	nitrogen-phosphorus (detector)
NTE	neuropathy target esterase
OECD	Organization for Economic Co-operation and Development
OP	organophosphorus pesticide
PHI	pre-harvest interval
ppm	parts per million. (Used only with reference to the concentration of a pesticide in a diet. In all other contexts the terms mg/kg or mg/l are used).
PT	prothrombin time
PTDI	provisional tolerable daily intake. (See 1994 report, Section 2.3, for explanation)
PTT	partial thromboplastin time
PTU	propylenethiourea
RAC	raw agricultural commodity
RBC	red blood cell
r.d.	relative density. (Formerly called specific gravity)
RfD	reference dose (usually in the phrase 'acute reference dose')
s.c.	subcutaneous
SC	suspension concentrate (= flowable concentrate)
SD	standard deviation
SE	standard error
SG	water-soluble granule
SL	soluble concentrate
SP	water-soluble powder
sp./spp.	species (only after a generic name)
SPE	solid-phase extraction
STMR	supervised trials median residue
t	tonne (metric ton)
T_3	tri-iodothyronine
T_4	thyroxine
TADI	Temporary Acceptable Daily Intake
tert	tertiary (in a chemical name)

TLC	thin-layer chromatography
TMDI	theoretical maximum daily intake
TMRL	Temporary Maximum Residue Limit
TRR	total radioactive residue
TSH	thyroid-stimulating hormone (thyrotropin)
UDMH	1,1-dimethylhydrazine (unsymmetrical dimethylhydrazine)
USEPA	United States Environmental Protection Agency
USFDA	United States Food and Drug Administration
UV	ultraviolet
WG	water-dispersible granule
WHO	World Health Organization
WP	wettable powder
<	less than
≤	less than or equal to
>	greater than
≥	greater than or equal to
*	at or about the limit of determination

USE OF JMPR REPORTS AND EVALUATIONS BY REGISTRATION AUTHORITIES

The summaries and evaluations contained in this book are, in most cases, based on unpublished proprietary data submitted for the purpose of the JMPR assessment. A registration authority should not grant a registration on the basis of an evaluation unless it has first received authorization for such use from the owner who submitted the data for JMPR review or has received the data on which the summaries are based, either from the owner of the data or from a second party that has obtained permission from the owner of the data for this purpose

INTRODUCTION

The report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Core Assessment Group (JMPR), held in Rome, 20-29 September 1999, contains a summary of the evaluations of residues in foods of the various pesticides considered as well as information on the general principles followed by the Meeting. The present document contains summaries of the residues data considered, together with the recommendations made.

The Evaluations are issued in two parts:

Part I: Residues (by FAO)
Part II: Toxicology (by WHO)

For those interested in both aspects of pesticide evaluation, not only both parts but also the reports containing summaries of reisude and toxicological considerations will be available. Special attention is drawn to Annex I containing updated ADIs, MRLs, and STMR levels which also appears in full as part of the report of the Meeting.

Some of the compounds considered at the Meeting have been previously evaluated and reported on in earlier publications. In general only new information is summarized in the relevant monographs and reference is made to previously published evaluations, which should also be consulted. In the case of older compounds which are re-evaluated as part of the periodic review programme of the CCPR a review of all available data, including data which may have previously been submitted, is carried out. Compounds evaluated for the first time are indicated by a single asterisk and those evaluated in the CCPR periodic review programme by double asterisks in the Table of Contents.

The name of the compound appearing as the title of each monograph is followed by its Codex Classification Number in parentheses.

References to previous Reports and Evaluations of Joint Meetings are listed in Annex II.

Acknowledgements

The monographs in these Evaluations were prepared by the following participants in the 1999 JMPR for the FAO Panel of Experts on Pesticide Residues in Food and the Environment:
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Note: Any comment on residues in food and their evaluation should be addressed to the:

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BENTAZONE (172)

EXPLANATION

The Meeting wished to clarify the statement in the report of the 1998 Joint Meeting (p. 53, last para) that "Metabolism studies in lactating goats and hens showed that the main residue component in meat, milk and eggs was the parent bentazone with small amounts of 6- or 8-hydroxybentazone and their glucuronide and sulfate conjugates."

APPRAISAL

The statement was based on the 1995 residue evaluation of the compound. Reconsideration of that evaluation indicated that the identified components of the residues in the milk and tissues of goats dosed with bentazone were bentazone and its *N*-glucuronide. "No 6-hydroxy-bentazone, 8-hydroxy-bentazone or AIBA (2-aminoisopropylbenzamide) could be found in the milk or tissues."[1] When hens were dosed with bentazone the main component of the residue in liver, muscle, fat and eggs was the parent compound. The liver contained bentazone (0.92 mg/kg) and its *N*-glucuronide conjugate (0.12 mg/kg). In the excreta 6-hydroxybentazone accounted for 15% of the radioactivity[2].

Residues of 6-hydroxybentazone and 8-hydroxybentazone and their sulfates were identified in the milk and tissues of goats dosed with the 6- and 8-hydroxy compounds, and 6-hydroxybentazone was found after dosing lactating goats with mixtures of bentazone and 6-hydroxybentazone.

It is emphasized that this clarification does not affect the conclusions of the 1998 Joint Meeting.

[1] 1995 residue evaluation, p. 9, para 4
[2] " " " , p. 11, penultimate para

BITERTANOL (144)

EXPLANATION

Bitertanol is an effective fungicide used preventively or curatively for the control of certain diseases in fruits and vegetables, e.g. scab and *Monilia laxa* in stone fruit, and as seed treatments against *Fusarium spp., Septoria, Tilletia caries* etc.

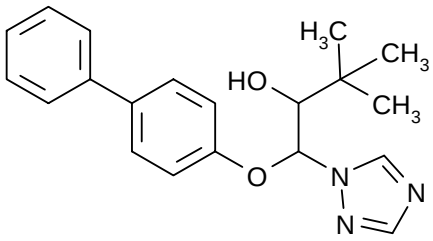
Bitertanol was originally evaluated in 1983 for toxicology and 1984 for residues. The compound was identified as a candidate for periodic re-evaluation at the 1996 CCPR (ALINORM 97/24, Annex 1) and scheduled for consideration by the FAO Panel of the 1999 JMPR at the 1997 CCPR (ALINORM 97/24A para 91, Appendix III).

The present Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP and residue trials from the manufacturer. Additional information on GAP and national MRLs was provided by Australia, Germany, Poland and the Netherlands, and on GAP by the UK.

IDENTITY

ISO Common name:	bitertanol
Chemical name:	
IUPAC:	1-(biphenyl-4-yloxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol (two diastereoisomers)
CA:	ß-([1,1'-biphenyl]-4-yloxy)-α-(1,1-dimethylethyl)-1*H*-1,2,4-triazole-1-ethanol 2 diastereoisomers, A (1*RS*, 2*SR*) and B (1*RS*, 2*RS*), approximately 70:30
Manufacturer's code number:	BAY KWG 0599
CAS number:	55179-31-2
CIPAC number:	386
Synonyms:	Baycor, Sibutol

Structural formula:



Molecular formula:	C_{20} H_{23} N_3 O_2
Molecular mass:	337.4 g/mol

PHYSICAL AND CHEMICAL PROPERTIES

A detailed chemical and physical characterization of the active ingredient is given in Table 1.
Test materials:

A Bitertanol diastereoisomer A, batch KRJ 061080 (purity 99.4 %)
B Bitertanol diastereoisomer B, batch KRJ 071080 (purity 99.7 %, data from 1981)
C Bitertanol diastereoisomer B, (high-melting form), batch KRJ 120387 (purity 99.15 %)
D Bitertanol diastereoisomer B, (low-melting form), batch KRJ 071080 (purity 97.4 %, data of 1989)
E Bitertanol, batch 940309ELB03 (purity 96.7 % (diastereoisomer A 77.7%, diastereoisomer B 19.0%)
F Bitertanol, batch APF 13028501 (purity 98.7 %)

Table 1. Physical and chemical properties of bitertanol.

Property	Characteristics	Test material	Reference
Physical state, colour	white to grey powder		Bayer AG, 1998
Odour	weak, characteristic		Bayer AG, 1998
Vapour pressure	Diastereoisomer A: 2.2×10^{-10} Pa at 20 °C 8.0×10^{-10} Pa at 25 °C diastereoisomer B: 2.5×10^{-9} Pa at 20 °C 7.5×10^{-9} Pa at 25 °C	A B	Herrmann, 1981a Herrmann, 1981b
Melting point	Diastereoisomer A: 138.6 °C diastereoisomer B (high-melting form): 147.1 °C (after heat treatment) diastereoisomer B (low-melting form): 125.8 °C (after heat treatment)	A, C, D	Krohn, 1989
Partition coefficient n-octanol/ water	Diastereoisomer A: log Pow = 4.04 at 20 °C, pH 2-9 diastereoisomer B: log Pow = 4.15 at 20 °C, pH 2-9	E	Krohn, 1996
Solubility in water	Diastereoisomer A: 2.7 mg/l at 20°C diastereoisomer B: 1.1 mg/l at 20°C sum of A + B: 3.8 mg/l at 20°C	E	Krohn, 1996
Solubility in organic solvents (at 20 °C, in g/l)	A / B / A + B n-heptane 0.30 / 0.14 / 0.44 xylene 16 / 1.8 / 18 dichloromethane / / >250 2-propanol 41 / 26 / 67 1-octanol 35 / 18 / 53 polyethylene glycol 65 / 56 / 120 acetone 127 / 74 / 200 ethyl acetate 92 / 59 / 150 acetonitrile 51 / 28 / 79 dimethyl sulfoxide / / >250	E	Krohn, 1996
Relative density	data on the pure active ingredient not available; technical material: 1.19 20°C/4°C		Mobay Chemical Corporation, 1984e
Hydrolysis rate	0.25 mg/l and 2.5 mg/l bitertanol in sterile aqueous buffer (pH 4, 7, 9) at 25°C and 40°C: no degradation after 30 days		Nichol and Thornton, 1979
Photochemical degradation	half-life in aqueous solution under natural sunlight approximately 11 days		Sietsema, 1983
Dissociation constant	Bitertanol does not show basic or acidic properties in water. It is not possible to specify a dissociation constant in aqueous solution.	E	Stupp, 1996

Property	Characteristics	Test material	Reference
Temperature of decomposition or sublimation	Diastereoisomers A and B thermally stable at room temperature.	F	Klusacek, 1986
Volatility	Henry's law constant at 20 °C (calculated) Diastereoisomer A: 2.3 x 10^{-10} [hPa x m³/mol] diastereoisomer B: 5.3 x 10^{-9} [hPa x m³/mol]		Krohn, 1992

Formulations

Bitertanol

300 EC	emulsifable concentrate containing 300 g/l bitertanol
500 SC	suspension concentrate containing 500 g/l bitertanol
25 WP	wettable powder containing 250 g/kg bitertanol

Combinations of bitertanol with other pesticides

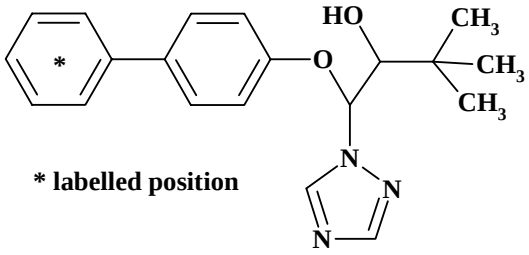
39.8 DS	powder for dry seed treatment containing 37.55 bitertanol + 2.3% fuberidazole
535.9 FS	flowable concentrate for seed treatment containing 33.8% bitertanol + 2.1% fuberidazole
199 FS	flowable concentrate for seed treatment containing 187.5 g/l bitertanol + 11.5 g/l fuberidazole
286 FS	flowable concentrate for seed treatment containing 188 g/l bitertanol + 23 g/l fuberidazole + 75 g/l triadimenol
325 FS	flowable concentrate for seed treatment containing 75 g/l bitertanol + 250 g/l anthraquinone
337.5 FS	flowable concentrate for seed treatment containing 37.5 g/l bitertanol + 125 g/l anthraquinone + 175 g/l imidacloprid
375 FS	flowable concentrate for seed treatment containing 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole
398 FS	flowable concentrate for seed treatment containing 375 g/l bitertanol + 23 g/l fuberidazole
398.5 FS	flowable concentrate for seed treatment containing 375.2 g/l bitertanol + 23.3 g/l fuberidazole
10 LA	lacquer containing 10 g/l bitertanol + 10 g/l 8-hydroxyquinoline sulfate
236.1 LS	solution for seed treatment containing 140 g/l bitertanol + 8.6 g/l fuberidazole + 87.5 g/l imidacloprid
298 LS	solution for seed treatment containing 280 g/l bitertanol + 18 g/l fuberidazole
55 WP	wettable powder containing 5% bitertanol + 50% captan
68.75 WP	wettable powder containing 7.5% bitertanol + 60% captan + 1.25% triadimenol
72.5 WP	wettable powder containing 12.5% bitertanol + 60% captan

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rat biokinetics

Bitertanol uniformly labelled with ^{14}C in the second ring of the biphenyl moiety was administered orally



*** labelled position**

to male and female rats at a dose level of 10 mg/kg (Klein, 1988a). Radioactivity was determined in the excreta and plasma as a function of time and the individual organs and tissues as well as the carcase were finally assayed for total radioactivity. Male rats were also administered the same dose

intraduodenally after bile fistulation and radioactivity was assayed in the excreta, including the bile, and in the body at death. A summary of the biokinetic data is given in Table 2.

After oral administration most of the radioactivity was absorbed. After intraduodenal administration of 10 mg/kg to the bile-fistulated male rats the recovered radioactivity in the urine, bile, and body excluding the gastrointestinal tract accounted for about 81%. Absorption commenced immediately, and the plasma concentration increased from 25 to 75% of the peak value within one to two hours, depending on the sex.

The radioactivity was almost completely excreted with the urine and faeces within the 72-hour test period. More than 90% of the recovered radioactivity was excreted with the faeces, and only about 7% with the urine. On average, the residual radioactivity in the body excluding the gastro-intestinal tract at death amounted to about 0.5% of the administered dose, and that in the gastrointestinal tract to about 0.1%.

From the results of the bile fistulation experiment it could be concluded that most of the faecally eliminated radioactivity was first absorbed and then eliminated into the gut lumen with the bile, mainly after entering the enterohepatic circulation.

Table 2. Recovery of radioactivity as percentage of the administered dose (Klein, 1988a).

Sample	Route and sex		
	Oral, male	Oral, female	Intraduodenal, male
Bile			77.00
Urine	7.74	6.21	3.76
Faeces	92.16	85.77	14.19
GI-Tract	0.10	0.15	0.02
Body exc. GI-Tract	0.46	0.58	0.46
Recovery	100.46	92.71	95.42

The radioactivity was rapidly distributed from the intravascular space to the peripheral tissues. The maximum dose-normalized concentration of radioactivity in the plasma was reached after three to eight hours. The terminal elimination of radioactivity from the plasma was determined by linear regression analysis, which showed a half-life of about 26 hours.

Table 3 shows the radioactivity levels determined in the individual organs and tissues after oral doses at the end of the test period (72 hours); the highest concentrations were found in the liver and kidneys.

Table 3. Dose-normalized concentrations of total radioactivity in organs and tissues of rats 72 h after single oral doses of 10 mg/kg (Klein, 1988a).

Sample	Male rats			Female rats		
	P[1], mean	cv, %	n	P[1], mean	cv, %	n
Erythrocytes	0.00451	7	5	0.00409	19	5
Spleen	0.00227	15	5	0.00321	21	5
GI-Tract	0.01025	35	5	0.01369	46	5
Liver	0.07322	12	5	0.09844	26	5
Kidneys	0.03713	10	5	0.03623	39	5
Testicles	0.00082	17	5			
Ovaries				0.00658	45	5
Uterus				0.00235	37	5
Muscle	0.00070	10	5	0.00075	12	5
Bone	0.00075	5	5	0.00073	19	5
Heart	0.00162	16	5	0.00166	17	5
Lung	0.00551	20	5	0.00785	28	5

Sample	Male rats			Female rats		
	P[1], mean	cv, %	n	P[1], mean	cv, %	n
Brain	0.00052	19	5	0.00155	44	5
Skin	0.00164	10	5	0.00240	16	5
Carcase	0.00104	10	5	0.00141	16	5
Fat	0.00091	26	4	0.00114	37	5
Plasma	0.00187	16	5	0.00184	26	5
Body excl. GI-Tract	0.00511	13	5	0.00649	20	5

[1] (radioactivity measured per g sample)/(radioactivity administered per g body weight)

Rat metabolism

The biotransformation of bitertanol was also studied by Klein (1988b, 1991). Metabolites were determined in the faeces, urine and bile, as well as in the liver, kidneys and perirenal fat at various times after dosing.

It was shown that metabolism commenced immediately after absorption from the lumen of the gastrointestinal tract. The parent compound was not detected in either urine or bile. The only metabolite identified in the bile was *p*-hydroxybitertanol. Excretion of the unchanged parent compound in the urine was unlikely owing to its lipophilic character. Metabolic degradation in the organs was also rapid: the bitertanol level in the liver fell from about 15 to 2% of the total organ radioactivity within eight hours. The main metabolite in the liver was also *p*-hydroxybitertanol, with smaller amounts of *p*-hydroxybitertanol acid, *p*-hydroxybitertanol alcohol, and bitertanol acid. The kidneys showed almost identical results: the percentage of total organ radioactivity fell from about 14 to 2.5% within eight hours. The major metabolite in the kidneys was again *p*-hydroxybitertanol, amounting to about 30 to 50% of the organ radioactivity. The other metabolites found in the liver were also present in the kidneys at similar levels.

The total radioactivity in the fat samples was too low to permit reliable quantification or identification of possible metabolites. This was mainly owing to the small amount of fat available in the young adult test animals.

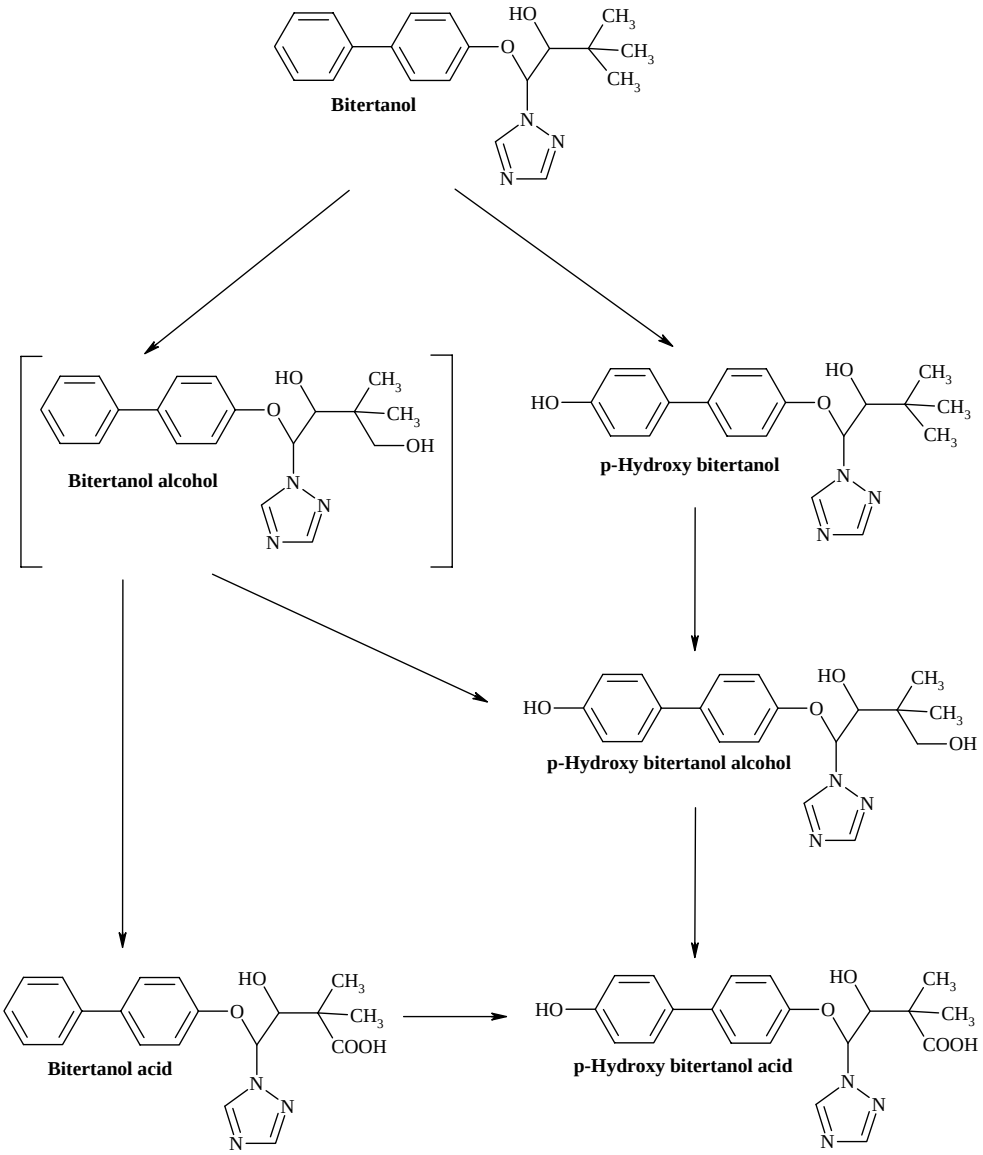
The presence of the parent compound in the faeces of orally treated rats can probably be explained by the unabsorbed fraction of administered radioactivity, amounting to approximately 15% of the dose. The main metabolite in the liver and kidneys, *p*-hydroxybitertanol, could also be identified in the faeces. The amounts of the other biotransformation products found in the organs were probably too low for detection in the excreta. The distribution of the identified metabolites in the faeces, liver and kidneys is shown in Table 4.

Table 4. Identified compounds in faeces, liver and kidneys as % of total ^{14}C at various times after oral administration of 10 mg/kg bitertanol (Klein, 1988b, 1991).

Compound	Faeces		Liver				Kidneys			
	male	female	Male at				Male at			
	at 48 h		40 min	2 h	4 h	8 h	40 min	2 h	4 h	8 h
bitertanol	16.7	13.0	15.2	6. 6	2.6	1.9	14.2	6.0	4.5	2.5
p-OH-bitertanol	2.1	2.2	33.2	38.0	23.2	25.0	32.4	35.1	46.9	48.9
p-OH-bit. alcohol			5.2	3.8	7.4	7.4	3.2	3.0	2.8	2.6
bitertanol acid			5.4	4.5	1.7	1.3	2.9	2.3	2.2	4.0
p-OH-bit. acid			3.5	3.0	---	---	3.0	---	2.2	---
Total identified			62.5	55.7	34.8	35.5	55.6	46.3	58.9	57.9

Proposed metabolic pathways of bitertanol in rats are shown in Figure 1.

Figure 1. Proposed metabolic pathways of bitertanol in rats after oral administration of 10 mg/kg (Klein, 1991).



The absorption, excretion, and metabolism of [U-*phenyl*-^{14}C]bitertanol was investigated in rats under various dosing conditions as follows (Puhl and Hurley, 1983)

Group A: single intravenous radiolabelled dose at 100 mg/kg
Group B: single oral radiolabelled dose at 100 mg/kg
Group C: fourteen daily oral unlabelled doses chemical followed by a single oral radiolabelled dose in each case at 100 mg/kg
Group D: single oral radiolabelled dose at 1000 mg/kg

The absorption of radioactivity was found to depend on the dose. Its elimination was mainly in the faeces with urinary radioactivity representing only 4-11% of the dose. Seven days after dosing, 0.2-0.4% of the dose remained in the body. Bitertanol was extensively metabolized, with similar metabolite profiles in the various groups. The relative levels of metabolites were also similar, except that the animals receiving the highest oral dose eliminated much more unchanged parent compound than the others. A total of 14 metabolites plus bitertanol, representing a total of 38-76% of the recovered radioactivity were identified or characterized (Table 5). The metabolic reactions included ring hydroxylation and di-

hydroxylation, aryl *O*-methylation, aliphatic hydroxylation, aliphatic oxidation to the tertiary carboxylic acid, and ether cleavage.

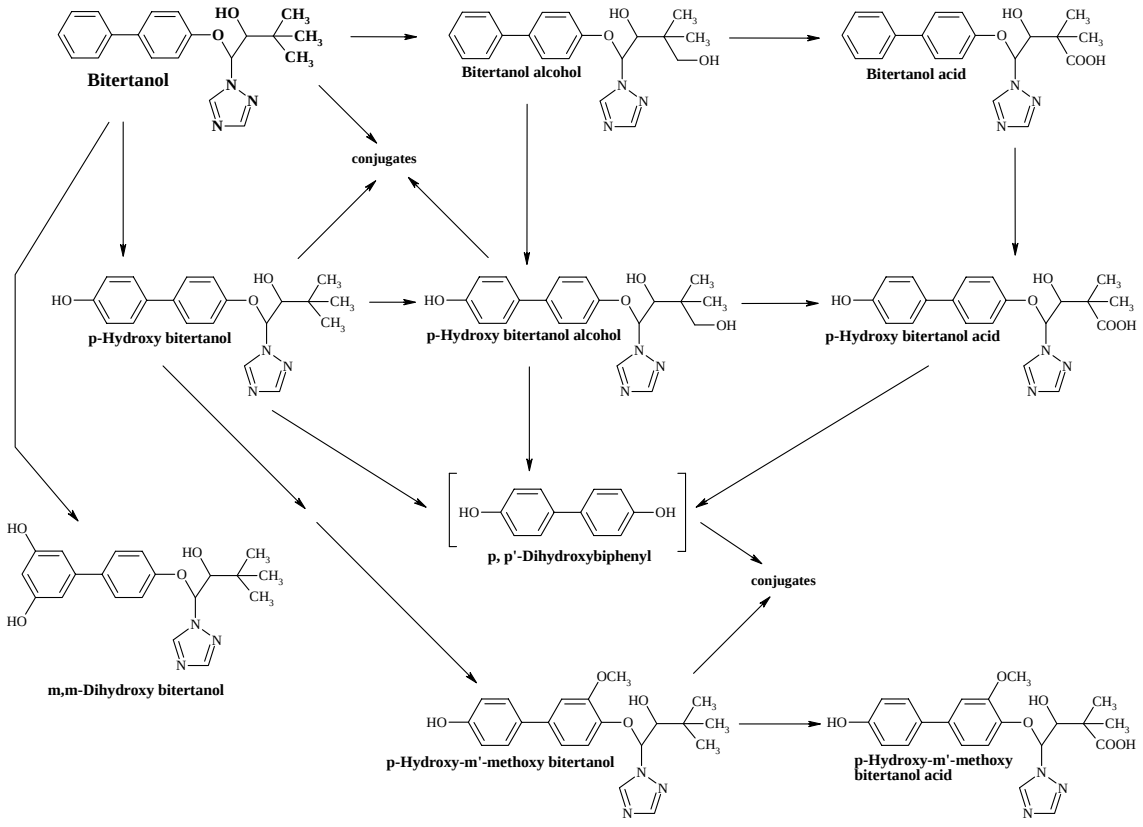
Table 5. Identified compounds in the excreta of rats (Puhl and Hurley, 1983).

Compound	% of recovered radioactivity							
	100 mg/kg i.v.		100 mg/kg oral		100 mg/kg oral		1000 mg/kg oral	
	Single dose		Single dose		Multiple doses		Single dose	
	Male	female	male	female	male	female	male	female
bitertanol	1.8	1.4	8.5	4.3	6.8	2.9	55.3	59.1
p-hydroxybitertanol	8.6	7.5	7.2	6.6	4.6	5.5	3.9	3.0
p-hydroxybitertanol alcohol	4.2	3.1	5.6	5.1	6.3	3.3	1.7	1.6
bitertanol acid	4.9	2.5	3.1	3.4	4.2	3.5	1.3	1.3
p-hydroxybitertanol acid	11.6	9.1	6.6	10.2	5.6	9.2	4.7	4.2
m,m-dihydroxy bitertanol	3.8	8.4	5.2	9.9	6.4	9.0	2.1	3.3
p-hydroxy-m'-methoxybitertanol	3.2	1.9	5.1	2.1	0.2	0.1	1.7	0.9
bitertanol alcohol	1.5	1.2	1.6	1.0	1.0	1.2	0.7	0.3
p-hydroxy-m'-methoxybit. acid	1.6	---	1.0	---	1.1	---	0.6	---
Conjugates*	2.6	3.6	2.1	2.5	2.0	3.3	1.5	1.8
Total	43.8	38.7	46.0	45.1	38.2	38.0	73.5	75.5

*Glucuronide or sulfate

The metabolic reactions in rats under these conditions are shown in Figure 2.

Figure 2. Reaction pathways involved in metabolism of bitertanol in rats after oral administration of 100 and 1000 mg/kg doses (Puhl and Hurley, 1983).



The absorption, excretion, and metabolism of [U-*phenyl*-^{14}C]bitertanol was investigated in male and female rats after a single oral dose of 100 mg/kg (Puhl *et al.*, 1979).

The results were similar to those found later and described above. The administered radioactivity was completely eliminated within 7 days. About 92% of the dose was found in the faeces and about 8% in the urine. The liver and kidneys showed the highest tissue residue levels. The unchanged parent compound constituted 8-11% of the excreted radioactivity. Chemical and spectral examination of some of the other components indicated that bitertanol underwent mono- and dihydroxylation of the biphenyl ring and hydroxylation at the *tert*-butyl group. In this early report structures were not identified.

Ruminant metabolism

The metabolism and excretion of [U-*phenyl*-^{14}C]bitertanol was investigated in a dairy cow after oral administration of 0.2 mg/kg bw. The excretion and tissue levels were described by Obrist *et al.* (1981) and the complete data including the metabolism results were given by the same authors in a second report (1983). In the first experiment, a single oral dose of 0.2 mg/kg bw was administered to a lactating dairy cow. Of the recovered radioactivity, 82.8% was in the faeces, 9.3% in the urine, and 0.2% in the milk. The residues in the milk did not exceed 0.009 mg/kg as bitertanol. The main metabolic pathway involved monohydroxylation of the phenyl ring. Minor reactions included hydroxylation and oxidation of the *tert*-butyl group, ring dihydroxylation, aryl *O*-methylation, ether cleavage, and conjugation. Thus, the major metabolites in the urine, faeces and milk were the diastereoisomers of *p*-hydroxybitertanol and their conjugates. The identified residues in the faeces and urine together represented about 75% of the excreted radioactivity (Table 6). The blood levels peaked at 0.013 mg/kg (bitertanol equivalents) 12.5 hours after dosing.

Table 6. Compounds identified in fractions of urine, faeces and milk after oral administration of [U-*phenyl*-^{14}C]bitertanol to a dairy cow at 0.2 mg/kg bw (Obrist *et al.*, 1981, 1983).

Compound	^{14}C as % of excreted		^{14}C as % of total milk residue
	Urine	Faeces	Milk
bitertanol	0.2	12.3	35.2
p-hydroxybitertanol	2.2	39.2	48.8
p-hydroxy-*m*'-methoxy bitertanol	0.3	0.2	---
bitertanol alcohol	0.4	3.6	8.5
p-hydroxybitertanol alcohol	0.5	6.7	2.1
bitertanol acids	0.8	---	---
p-hydroxybitertanol acid	0.5	---	---
p-hydroxybiphenyl	0.7	2.6	2.9
p,p'-dihydroxybiphenyl	3.5	1.2	---
polar metabolites	---	15.3	---
Unextractable	---	4.1	---

In a subsequent experiment, the same animal was treated with five daily doses of 0.2 mg/kg bw [U-*phenyl*-^{14}C]bitertanol, and killed 12.5 hours after the last dose. Tissue residues were 0.82 mg/kg (bitertanol equivalents) in the liver, 0.11 mg/kg in the kidneys, 0.03 mg/kg in fat and 0.01 mg/kg in muscle. The recovered radioactivity in the milk did not exceed 0.2% of the applied ^{14}C, and multiple dosing did not result in increased residues (the final residue was 0.008 mg/kg as compared with a maximum of 0.009 mg/kg in the single-dose experiment). Prominent metabolites in the tissues included *p*-hydroxybitertanol, bitertanol alcohol, *p*-hydroxybitertanol alcohol, and *p,p*'-dihydroxybiphenyl. The results are summarized in Table 7.

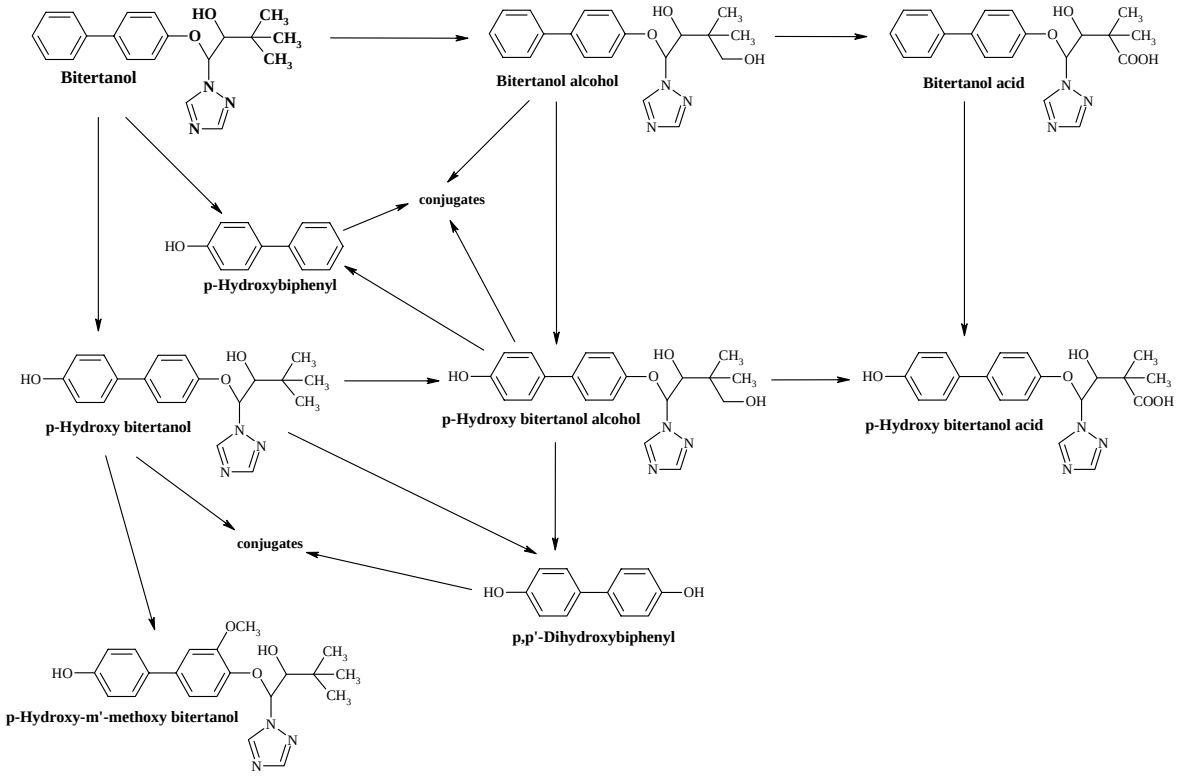
Table 7. Compounds identified in fractions of tissues from a dairy cow taken 12.5 hours after five daily oral doses of [U-*phenyl*-^{14}C]bitertanol**,** 0.2 mg/kg bw per dose (Obrist *et al.*, 1981, 1983).

Compound	^{14}C, % of total residue					
	Liver A*	Liver B*	Kidneys A*	Kidneys B*	Muscle	Fat
Bitertanol	6.8	6.8	5.7	5.7	13.6	25.0
p-hydroxybitertanol	24.5	39.6	17.6	19.5	37.7	18.6
p-hydroxy-*m*'-methoxy bitertanol	3.1	4.1	2.7	2.7	---	---
Bitertanol alcohol	0.9	0.9	4.8	4.8	14.0	7.1
p-hydroxybitertanol alcohol	2.1	2.7	5.4	5.4	12.4	9.2
p-hydroxybiphenyl	---	0.8	4.0	2.3	3.6	7.9
p,p'-dihydroxybiphenyl	---	1.0	4.2	2.8	5.3	11.7
Unextractable	30.5	30.5	33.0	33.0	< 0.1	9.2

A* The residue remaining from the methanol extract after evaporation was partioned between hexane and acetonitrile.
B* The residue remaining from the methanol extract after evaporation was solubilized with a sodium acetate buffer and incubated with glusulase. After extraction of the incubate with dichloromethane/acetonitrile (2:1), the residue in the organic phase was partioned between hexane and acetonitrile.

The metabolic reactions in the dairy cow are shown in Figure 3.

Figure 3. Major reaction pathways in metabolism of bitertanol in the dairy cow (Obrist *et al.*, 1983).



Poultry metabolism

The metabolism and excretion of [U-*phenyl*-^{14}C]bitertanol were investigated in 3 groups of laying hens (Obrist and Puhl, 1986).

Group A: Five birds given a single oral dose at 2.5 mg/kg bw for determination of excretion pattern.

Group B: Ten birds given a single oral dose at 2.5 mg/kg bw for determination of blood levels.

Group C: Three birds given 5 daily doses at 8.0 mg/kg bw (equivalent to 90 ppm in feed) for investigation of tissue residues.

Group A showed the elimination of 98% of the dose with the excreta and 0.2% in the eggs over a period of four days. The major metabolites in the excreta were the diastereoisomers of *p*-hydroxybitertanol and their conjugates. The proportion of totally identified radioactivity in the excreta was 86%, and 84% of the egg residue was identified. The total radioactive residues in the tissues were 0.1 mg/kg as bitertanol four days after dosing. Blood levels peaked 0.5-1 hour after administration. Analyses of tissues collected 45 minutes after the last of five daily doses resulted in identification of 81% of the liver residue and 86-92% of the residues in the other tissues.

It can be concluded that bitertanol is intensively metabolized and rapidly excreted by laying hens. The major metabolic pathway involves hydroxylation of the phenyl ring followed by sulfuric or glucuronic acid conjugation. Minor metabolic reactions include hydroxylation of the *tert*-butyl group, dihydroxylation of the biphenyl ring system, *O*-methylation and conjugation. Metabolites are not retained by the tissues, as shown by the low residues ($\leq$0.1 mg/kg) four days after a single dose. The distribution of the identified compounds in the edible tissues and eggs is shown in Tables 8 and 9 respectively.

Table 8. Identified compounds in edible tissues taken 45 minutes after the last of five daily doses of [U-*phenyl*-^{14}C]bitertanol to three laying hens at 8.0 mg/kg bw (Obrist and Puhl, 1986).

Compound	^{14}C, % of total residue				
	Liver	Kidneys	Muscle	Fat	Skin
bitertanol	34.7	27.2	67.8	78.2	74.9
p-hydroxybitertanol, free	14.7	27.7	23.2	12.1	13.2
p-hydroxybitertanol, conjugated[1]	25.4	24.8	1.5	---	4.2
p-hydroxybitertanol alcohol glucuronide	0.4	0.9	---	---	---
	0.2	---	---	---	---
Bitertanol alcohol glucuronide	1.2	1.8	---	---	---
	0.8	1.1	---	---	---
p-hydroxybiphenyl	0.2	0.2	---	---	---
p,*p*'-dihydroxybiphenyl	0.7	0.2	---	---	---
dihydroxybitertanol	0.9	---	---	---	---
hydroxymethoxybitertanol	1.7	2.2	---	---	---
polar metabolites	4.4	4.4	0.5	---	---
Unextracted	7.2	1.9	2.6	6.8	5.3

[1]Sulfate, glucuronide, others

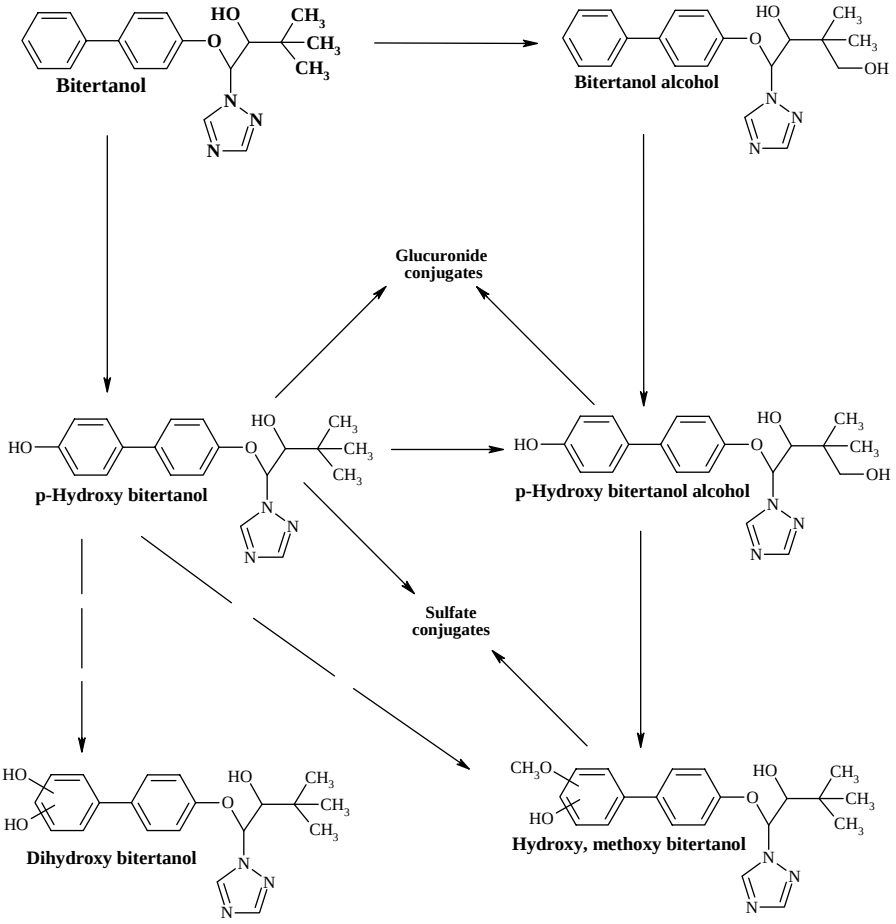
Table 9. Identified compounds in eggs after the administration of single or multiple oral doses of [U-*phenyl*-^{14}C]bitertanol to laying hens (Obrist and Puhl, 1986).

Compound	^{14}C, % of total residue in eggs	
	Single dose 2.5 mg/kg bw	Multiple doses 5 x 8.0 mg/kg bw
bitertanol	54.8	36.6
p-hydroxybitertanol, free	6.3	6.4
p-hydroxybitertanol, conjugated[1]	21.6	37.9
p-hydroxybitertanol alcohol	0.4	0.3
bitertanol alcohol	0.6	0.5
p,*p*'-dihydroxybiphenyl	---	1.3
hydroxymethoxybitertanol	0.6	1.0
polar metabolites	0.5	1.2
Unextracted	8.4	6.7

[1]Sulfate, glucuronide

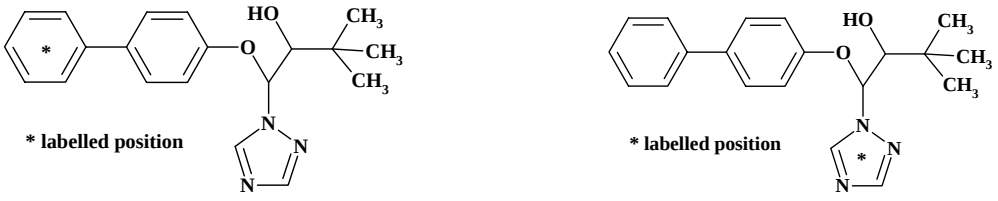
The metabolic reactions in poultry are shown in Figure 4.

Figure 4. Metabolism of bitertanol in poultry (Obrist and Puhl, 1986).



Plant metabolism

The metabolism of bitertanol was investigated in apples, peanuts and cotton after spray application and in spring wheat after seed dressing with biphenyl- and triazole-labelled compounds. The labelled positions are shown below.



The two diastereoisomers are referred to as forms I and II in these studies. Form I is defined as the isomer having the lower R_f value on silica gel TLC with ethyl acetate as mobile phase.

Apples. [U-*phenyl*-^{14}C]bitertanol as a 50% WP was applied to apple surfaces at a concentration corresponding to 0.015% ai (Puhl and Hurley, 1981a). The compound was slowly metabolized with a half-life of approximately 150 days. The two diastereoisomers were metabolized at similar rates. After 21 and 49 days 90 and 86% respectively of the total apple residue was identified. Bitertanol

constituted 83% at 49 days while the keto-analogue of bitertanol (BUE 1662) and 4-hydroxybiphenyl together contributed 3%. The overall bitertanol isomer ratio changed little with time indicating similar rates of metabolism for the two isomers. Only 2% of the radioactive residue remained in the aqueous fractions, while 9.8% remained unextracted. After 49 days only 5% of the residue had penetrated into the pulp. The authors provide ample evidence from the literature that the unextracted radioactivity is not bioavailable to mammals after ingestion since it is probably associated with high molecular weight materials which are not readily digestible.

The results with the triazole-labelled active ingredient were very similar (Pither and Stevenson, 1987a). After spray application of a 50% WP formulation to apples, bitertanol was metabolized only very slowly. The degradation was less than 5% after 49 days (mature harvest) with very little penetration of the radioactivity into the pulp. 9.1% of the recovered radioactivity was detected in the washed peel. Most of the radioactivity associated with the peel and pulp fractions was extractable with organic solvents: only 2.5 and 0.3% of the total radioactive residue was unextractable from the peel and pulp samples respectively, and 95.6% of the recovered residue was identified as unchanged bitertanol.

Peanuts. The metabolism of [U-*phenyl*-^{14}C]bitertanol in peanuts was investigated after spray application and after root uptake from a nutrient solution.

After spray application to peanut plants at 560 g/ha bitertanol was slowly metabolized with an estimated half-life of 141 days (combined isomers). There was a significant difference in the degradation rate of the two isomers: bitertanol I was absorbed and metabolized with a half life of about 100 days and bitertanol II with a half life of about 300 days. Fractionation of shoot tissues 28 days after treatment of young plants showed that 96.5% of the radioactivity was organosoluble, of which 86.2% was bitertanol and 4.3% was tentatively identified by mass spectrometry as the 6-*O*-malonyl-β-D-glucoside of bitertanol I. Several other metabolites each represented less than 1% of the residue. Only 0.6% of the radioactivity was found in the aqueous and 2.9% in the solid fractions. The root residues were low as compared with those in the shoots, indicating that there was little basipetal movement of radioactivity. Nuts and shells harvested 2.5 months after a single foliar application both contained residues of 0.066 mg/kg bitertanol equivalents, corresponding to 0.008% of the total plant residue. The mature plants contained 75.1% bitertanol, 5.8% 6-*O*-malonyl-β-D-glucoside, and 19.1% unidentified radioactivity in organo- and water-soluble or unextractable fractions.

Administration of bitertanol by root uptake from a nutrient solution resulted in the absorption of 43.7% of the available compound in 7 days. The isomers were absorbed equally, but again isomer I was metabolized more rapidly than isomer II. 6-*O*-malonyl-β-D-glucoside was observed in all the experiments. Bitertanol does not appear to be translocated from old to new growth, nor to volatilize from the leaf surface.

Wheat. The metabolism and distribution of bitertanol in spring wheat after seed treatment was investigated in two trials with phenyl- and triazole-labelled test compounds applied at 75 g ai/100 kg seed (Brennecke, 1986). Samples were collected at three intervals after sowing, the third sample being taken at harvest.

The percentages of the recovered radioactivity at these sampling times were 0.3-2.8% in the aerial plant parts (forage, grain, glumes, straw), 29.4-70.1% in the roots (including seed), 12.1-41.5% in the top soil layer (0-5 cm), and 0.2-2.3% in the 5 to 10 cm soil layer. Losses of radioactivity varied between 17.3 and 31.8%. The total ^{14}C at harvest from the phenyl label was 0.26 mg/kg as bitertanol in straw, 0.08 mg/kg in grain, 20 mg/kg in roots, and 0.13 mg/kg in the top soil layer. From the triazole label the corresponding residues were 0.64 mg/kg in straw, 0.53 mg/kg in grain, 24 mg/kg in roots, and 0.20 mg/kg in the top soil layer.

Owing to the very low levels of radioactivity in many extracts, characterization and identification were possible only to a limited extent. The organic extracts of the top soil layer (59% biphenyl label, 83% triazole label) and the roots (66.5% biphenyl label, 74% triazole label) contained almost exclusively unchanged parent compound. The metabolites detected in the grain from the triazole label treatment were triazolylalanine (50-66%, 0.12–0.16 mg/kg), triazolylacetic acid (22-34%, 0.04-0.07 mg/kg) and 2-hydroxy-3-(1*H*-1,2,4-triazol-1-yl)propionic acid in traces (<1%, <<0.01 mg/kg). In straw these metabolites were present at lower concentrations than in grain (<0.01-0.03 mg/kg). Unchanged parent compound (approx. 6% or 0.038 mg/kg) and bitertanol benzoic acid (BUE 2684, 5.3%) were also identified.

The high levels of unextractable radioactivity in forage (about 70%) and straw (about 61%) were reduced by acid or enzymatic hydrolysis, but 52 and 40% of the radioactivity was still bound to forage and straw respectively, probably to the lignin fraction.

Cotton. Cotton plants in the early bloom stage were sprayed twice with triazole-labelled bitertanol at 250 g/ha. The spray interval was 14 days (Pither and Stevenson, 1987b).

In the mature plants 63 days after the second application, 91% of the recovered radioactivity was associated with the foliage and 5.5% with the calyx fraction; 1.3%, 1and 1% was found in the lint, seed and hull respectively. Most of the recovered residue was identified as the unchanged bitertanol isomers I and II, amounting to a total of 79% of the mature harvest residue. The relative concentrations of the bitertanol isomers remained constant throughout the study period. Trace amounts of bitertanol benzoic acid (BUE 2684) were identified at the interim sampling period of 35 days. Two further unknown metabolites were observed, collectively accounting for 1.3 and 0.3% of the 35-day and 63-day samples respectively.

Confined rotational crop study

[U-*biphenyl*-^{14}C]bitertanol was applied eight times as a foliar spray to a target crop of peanuts at 0.56 kg ai/ha per application. The peanuts were removed 31 days after the last application and part of the soil was planted with rotational crops of wheat, kale or mustard, and sugar beets. The remainder of the soil was planted with these rotational crops either 118 or 364 days after the final application. The rotational crops were analysed for radioactive residues at intervals up to harvest (Puhl *et al.*, 1982).

The radioactive residues in harvest samples of leafy vegetables (kale and mustard) ranged from 0.10 mg/kg as bitertanol (118-day rotation) to 0.02 mg/kg (364-day rotation). Harvest samples of sugar beet roots contained residues of 0.38 mg/kg (118-day rotation) to 0.01 mg/kg (364-day rotation), while residues in wheat heads ranged from 0.23 mg/kg (31-day rotation) to 0.01 mg/kg (364-day rotation).

Owing to the low residue concentrations, only limited identification was possible. Bitertanol was present in the 31-day wheat crop, as was bitertanol benzoic acid (BUE 2684). Organosoluble residues in harvest samples used for food or fodder were all below 0.05 mg/kg. Insoluble and water-soluble residues may have partly resulted from incorporation of soil-generated $^{14}CO_2$ into natural plant constituents.

The metabolic pathways of bitertanol in plants are shown in Figure 5 and the distribution of radioactive compounds in the crops and crop parts is shown in Table 10.

Figure 5. Proposed metabolic pathways of bitertanol in plants.

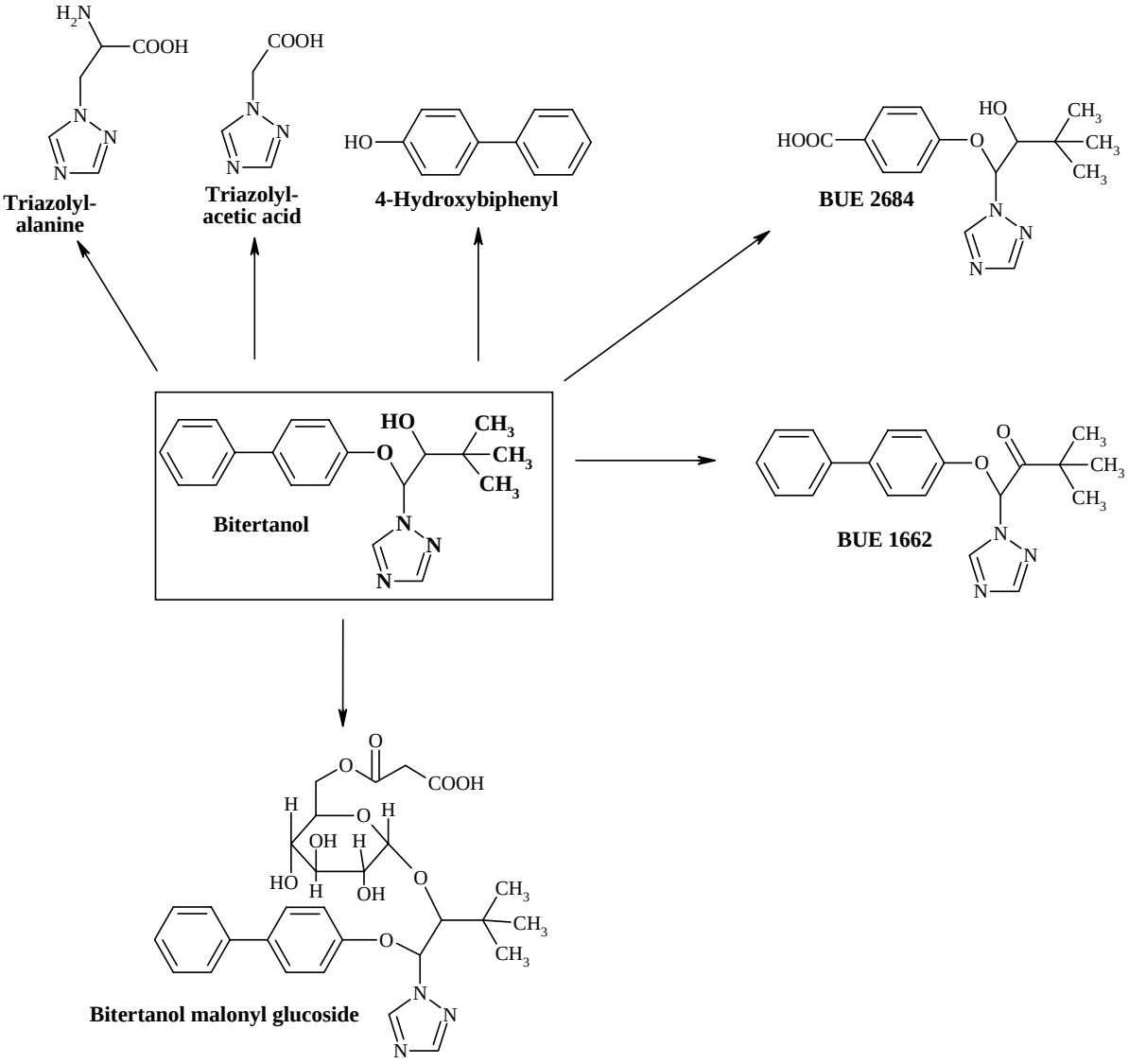


Table 10. Distribution of radioactive compounds in crops and crop parts after application of bitertanol.

Reference	Crop	Application rate, kg ai/ha ❶ or conc., % ●	Sample	Label	Days after application	TRR as bitertanol, mg/kg	Bitertanol, % of TRR	BUE 1662, % of TRR	4-OH-biphenyl, % of TRR	BUE 2684, % of TRR	TA, % of TRR	TAA, % of TRR	Malonyl glucoside, % of TRR	Unknown, % of TRR	Unextracted, % of TRR ÷
Puhl and Hurley, 1981a	Apple	0.015 ●	Fruit	Biphenyl	0 7 14 35 42 49	0.27 0.36 0.28 0.27 0.21 0.27	82.8 ❹	3.0 ❹a						4.4 ❹	9.8 ❹
Pither and Stevenson, 1987a	Apple	0.015 ●	Fruit	Triazole		nr	95.6 ❹							1.9 ❹	2.5 ❹
Puhl and Hurley, 1981b	Peanut	0.56 ❶	Shoots Roots	Biphenyl		nr	93.4 86.2 75.1						2.4 4.3 5.8	3.3 6.6 14.9	0.9 2.9 4.2
Brennecke, 1986	Wheat	75 g ai/100 kg ❺	Forage Grain Glumes Straw Roots Soil 0-5 cm Soil 5-10 cm	Biphenyl		0.13 ❼ 0.08 ❻ 0.30 ❻ 0.26 ❻ 20.35 ❻ 0.13 ❻ < 0.01 ❻	 66.5 ❻ 59.0 ❻								70.4 ❼ 90.6 ❻ 79.3 ❻ 61.2 ❻ 31.4 ❻ 38.0 ❻ 45.3 ❻
Brennecke, 1986	Wheat	75 g ai/100 kg ❺	Forage Grain Glumes Straw Roots Soil 0-5 cm Soil 5-10 cm	Triazole		0.42 ❼ 0.53 ❻ 0.29 ❻ 0.64 ❻ 23.92 ❻ 0.20 ❻ < 0.01 ❻	9.4 ❼ 5.9 ❻ 73.6 ❻ 83.4 ❻			 5.3 ❻	50-66 ❻	22-34 ❻			19.7 ❼ 5.7 ❻ 10.0 ❻ 46.2 ❻ 15.9 ❻ 14.3 ❻ 45.0❻
Pither and Stevenson, 1987b	Cotton	0.25 ❶	Leaves Calyx Lint Seed Hull	Triazole		91 5.5 1.3 1 1	78.8 |			0.2 —					15.2 |

nr: not reported

÷: not extractable by drastic procedures
❹: 49 days after application; a: sum of BUE 1662 and 4-OH-biphenyl
❺: seed dressing
❻: at harvest (95 or 100 days)
❼: at 36 or 49 days
|: at harvest (63 days)
—: at interim sampling (35 days)

BUE 1662: keto analogue of bitertanol
BUE 2684: bitertanol benzoic acid
TA: triazolylalanine
TAA: triazolylacetic acid

Environmental fate in soil

Photolysis

In a model experiment, bitertanol was spotted on two HPTLC plates, one of which was irradiated for six weeks while the other was shielded for the same period (Wilmes, 1980). With an error margin of the densitometric analyses of ± 10% photolytic degradation could not be reliably established, but the data suggest a slight degradation.

[U-*biphenyl*-^{14}C]bitertanol was applied to a silt loam soil and irradiated continuously with simulated sunlight for 35 days at 25°C and 55% relative humidity (Sietsema, 1982). Interim samples were taken at 7, 14, 21, and 28 days. At the end of the test period 91.5% of the extractable radioactivity from the irradiated samples was unchanged bitertanol as determined by thin-layer chromatography. No other discrete spots of radioactivity were visible in any of the chromatograms. 96.6% of the extractable radioactivity from the dark samples was from bitertanol. More than 90% of the ^{14}C in the irradiated and non-irradiated samples was extractable throughout the experiment. It is concluded that photodecomposition plays little part in the degradation of bitertanol on soil surfaces.

Adsorption/desorption

The adsorption of bitertanol by loam, silty clay and sand from solutions at initial concentrations of 1.6-13.6 mg/ml was studied by Puhl and Hurley (1979a). The results, which conformed well to the Freundlich equation, indicated that the compound is strongly adsorbed to soil, with K_{OC} values computed from the results of about 2000. Desorption was also determined. The results are shown in Tables 11 and 12.

Freundlich equation: $\log x/m = \log K + 1/n \log C$

x = bitertanol adsorbed, µg
m = mass of adsorbing soil, g
C = concentration in solution, µg/ml
K, n = constants

Table 11. Adsorption of bitertanol to soils after equilibration for 24 hours (Puhl and Hurley, 1979a).

Soil	Freundlich constants			C, µg/ml		Biteranol on soil, µg/g at equilibrium	% adsorbed
	K	1/n	r, %[1]	initial	at equilibrium		
Kansas loam	35.8	0.791	99.6	1.57	0.08	1.49	95
				3.33	0.17	3.16	95
				6.55	0.42	6.13	94
				13.60	1.17	12.43	91
Hagerstown silty clay	19.6	0.883	99.9	1.57	0.22	1.35	86
				3.33	0.50	2.83	85
				6.55	1.08	5.47	84
				13.60			
Florida sand	39.9	0.957	99.7	1.57	0.14	1.43	91
				3.33	0.36	2.97	89
				6.55	0.62	5.93	91
				13.60	1.40	12.20	90

[1] r = correlation coefficient describing the degree of conformity of the data with the Freundlich equation

Table 12. Desorption of bitertanol from soils (Puhl and Hurley, 1979a).

Soil	initial conc.	Freundlich constants			Bitertanol adsorbed to soil, µg/g		% desorbed
	[mg/kg	K	1/n	r , %[1]	after adsorption	after 4 desorptions	
Kansas Loam	0.16	2.18	0.225	95.1	1.49	1.43	4
	0.33	2.43	0.111	95.9	3.16	3.04	4
	0.66	7.62	0.282	97.5	6.13	5.86	4
	1.36	10.16	0.233	82.3	12.43	11.69	6
Hagerstorm silty clay	0.16	1.47	0.196	90.5	1.35	1.24	8
	0.33	2.58	0.191	93.8	2.83	2.59	8
	0.66	4.81	0.242	92.6	5.47	4.91	10
	1.36						
Florida sand	0.16	1.83	0.222	95.9	1.43	1.34	6
	0.33	2.91	0.198	79.7	2.97	2.79	6
	0.66	4.58	0.155	93.9	5.93	5.62	5
	1.36	7.69	0.116	94.0	12.20	11.61	5

[1] r = correlation coefficient describing the degree of conformity of the data with the Freundlich equation

In a recent study the adsorption/desorption of the possible soil degradation product bitertanol benzoic acid (BUE 2684) by loamy sand, sand, silty loam and silty clay was investigated at concentrations ranging from 0.01 to 5.0 mg/l. The percentage of the test compound adsorbed varied between 5.4 and 40.8%. The results indicated that the compound is highly mobile in soil since the K_{OC} values computed from the results were very low, from 6.06 to 15.37. In desorption experiments between 17.9 and 90.7% of the adsorbed bitertanol benzoic acid was desorbed (Burhenne, 1996).

Mobility

The distribution of [U-*phenyl*-^{14}C]bitertanol in soil after the seed treatment of winter wheat was investigated in a study under simulated winter climate conditions. When the plants reached the 3-leaf stage, only 0.32% of the applied radioactivity was recovered in the shoot while more than 99% remained in the soil, caryopsis and roots. Autoradiography demonstrated that the radioactivity was confined to the soil directly adjacent to the seed and did not move into deeper soil layers (Thielert and Kuck, 1992).

The leaching characteristics of aged [U-*phenyl*-^{14}C]bitertanol residues were studied in a sandy loam (Dutch polder) soil and a loamy sand (BBA standard soil 2.1) (Brennecke, 1983a). After fortification with bitertanol at a concentration of 10 mg/kg, the soils were incubated at 9°C and 22°C for 30 days and 105 days. The soil concentration corresponded to an exaggerated application rate of approximately 15 kg ai/ha. The proportion of the applied radioactivity mineralized to $^{14}CO_2$ after the ageing periods ranged from 2.1 to 68%. Leaching was induced in the soil columns containing the aged bitertanol residues by percolating water equivalent to 200 mm of rainfall for 48 hours. The application of simulated rainfall to the columns packed with the sandy loam soil was continued for an additional 72 hours, equivalent to 500 mm of precipitation.

The radioactivity in the leachates collected from the sandy loam soil accounted for only 0.2 to 0.6% of the applied dose after 48 hours of rainfall, and 1.0 to 2.8% after 120 hours. The leachates from the loamy sand contained 0.5 to 3.3% of the applied dose after 48 hours of simulated rainfall. In the total of 19 leaching experiments only one leachate sample from the loamy sand contained a higher proportion of the applied radioactivity (38.9%). It consisted almost quantitatively of bitertanol benzoic acid (BUE 2684); unchanged bitertanol was not found. Analysis of the soil columns after leaching showed that 84.2 to 86.0% of the radioactivity remaining in the soil was retained in the upper 5 cm layer. The overall average recovery of the radioactivity was 98.4%.

No essential differences in leaching characteristics were observed between the bitertanol residues aged at 22°C and those aged at 9°C in either soil. Prolongation of ageing from 30 days to 105 days reduced the radioactivity in the leachate (0.2-0.5% of the AR) from both soils because by

this time bitertanol had already been largely degraded to CO_2 (51 to 68%). The results show that aged bitertanol residues have only a limited tendency to leach into deeper soil layers (Tables 13 and 14).

Table 13. Radioactivity balance for aged [U-*phenyl*-^{14}C]bitertanol residues in soil (Brennecke, 1983a).

	Temp., °C	Duration of ageing, days	Radioactivity in soil , %	$^{14}CO_2$, %
NL polder soil	22	30	84.5	12.1
	22	105	50.0	51.4
	9	30	101.3	2.1
Standard soil 2.1	22	30	57.8	31.0
	22	105	34.4	68.0
	22	30	58.9	40.5
	9	30	88.3	5.0

Table 14. Leaching of aged [U-*phenyl*-^{14}C]bitertanol residues after simulated rainfall (Brennecke, 1983a).

	Temp., °C	Duration of ageing, days	Leachate, ml	Radioactivity in leachate , % *	**
NL polder soil (48 hours rainfall)	22	30	385	0.6	0.7
	22	105	410	0.2	0.5
	9	30	407	0.2	0.2
Standard soil 2.1 (48 hours rainfall)	22	105	368	0.5	1.7
	22	30	397	1.0	1.8
	9	30	410	3.3	3.5
NL polder soil (120 hours rainfall)	22	30	965	2.8	3.1
	22	105	1023	1.0	2.1
	9	30	1013	1.1	1.2

* Applied radioactivity (AR) = 100 %
** Radioactivity in soil (AR-$^{14}CO_2$) = 100 %

Bitertanol was spotted on TLC plates coated with six different types of soil ranging from non-adsorptive sand to fine clay (Obrist and Thornton, 1979). Development of the plates with distilled water showed that bitertanol could be classified as being of low mobility.

Degradation

A laboratory study of aerobic degradation was conducted with [U-*phenyl*-^{14}C]bitertanol on four agricultural soils: sand, loamy sand, silt loam and silt (Fent, 1997). The application rate corresponded to 560 g ai/ha and the soils were incubated for 120 days. Samples were taken after 0, 3, 7, 14, 22, 30, 60, 90, 100, and 120 days.

The test substance was rapidly degraded with initial half-lives <1 day to 9 days. At the end of the test period the degradation curve flattened, giving DT-90 values of 15 to 102 days. The main product after 120 days was $^{14}CO_2$, representing 50 to 64% of the applied radioactivity. Bitertanol benzoic acid (BUE 2684) was the only other identified product, detected only in trace amounts, less than 0.3% of the applied radioactivity, in two of three extracts after concentrating them. Less than 4.2% of the AR remained unidentified. Unextracted residues, which were bound to the stable humin fraction, increased within the first 22 days to about 30-50% of the applied ^{14}C. After that period the unextractable residues decreased slightly in all the soils, indicating that a part of the bound residues became bioavailable again and thus subject to mineralization. The recovery ranged from 90.6 to 110% of the applied radioactivity. The results are shown in Tables 15 and 16.

Table 15. DT-50 and DT-90 values of bitertanol in soils (Fent, 1997).

Soil		DT-50, days	DT-90, days
BBA 2.1	(sand)	4.97	54.90
BBA 2.2	(loamy sand)	9.23	101.9
Laacher Hof	(silt loam)	4.00	44.15
Höfchen	(silt)	0.56	15.30

Table 16. Distribution of radioactivity, as % of that applied, after aerobic incubation of [U-*phenyl*-^{14}C]bitertanol on four different soils (Fent, 1997).

Days	Bitertanol	BUE 2684	$^{14}CO_2$	Unidentified	Unextracted	Total
	Soil BBA 2.1					
0	109.2	0.0	0.0	0.1	0.8	110.1
3	99.8	0.0	1.1	0.5	4.5	105.9
7	81.0	0.0	4.5	1.1	11.9	98.5
14	42.7	0.0	10.4	1.8	25.2	80.1
22	22.6	0.0	43.6	2.1	30.5	98.8
30	14.0	0.0	52.0	1.5	29.8	97.3
60	8.6	0.0	54.1	1.5	26.4	90.6
90	6.9	0.0	64.7	1.5	25.9	99.0
100	6.5	0.0	59.0	1.3	24.8	91.6
120	5.2	0.0	63.6	1.1	23.2	93.1
	Soil BBA 2.2					
0	104.4	0.0	0.0	0.1	0.0	104.5
3	87.4	0.0	1.5	2.9	10.7	102.5
7	55.3	0.2	11.2	4.2	24.6	95.5
14	32.6	0.0	12.8	2.6	34.2	82.2
22	26.8	0.0	32.5	3.8	38.1	101.2
30	20.0	0.0	37.3	2.0	39.5	98.8
60	13.8	0.0	42.1	1.9	37.0	94.8
90	10.6	0.0	48.3	1.9	38.8	99.6
100	10.9	0.0	48.0	1.8	38.4	99.1
120	9.8	0.0	51.3	1.4	36.7	99.2
	Soil Laacher Hof					
0	108.0	0.0	0.0	0.1	0.8	108.9
3	80.5	0.3	2.4	1.5	16.8	101.5
7	50.5	0.0	7.6	1.6	31.0	90.7
14	21.1	0.0	23.7	2.1	41.8	88.7
22	10.0	0.0	43.2	1.5	43.6	98.3
30	8.6	0.0	44.2	1.6	43.0	97.4
60	4.9	0.0	51.7	1.2	38.8	96.6
90	3.6	0.0	54.0	1.2	38.7	97.5
100	3.4	0.0	53.1	1.2	39.8	97.5
120	3.2	0.0	56.4	1.0	36.8	97.4
	Soil Höfchen					
0	104.3	0.0	0.0	0.1	1.1	105.5
3	59.9	0.0	3.4	3.5	25.2	92.0
7	29.4	0.0	18.0	2.7	41.1	91.2
14	13.5	0.0	29.4	2.8	46.2	91.9
22	6.9	0.0	40.1	2.5	48.8	98.3
30	6.2	0.0	43.3	2.0	45.7	97.2
60	4.2	0.0	47.2	1.8	44.2	97.4
90	3.0	0.0	51.0	1.6	42.6	98.2
100	2.9	0.0	51.6	1.4	42.6	98.5
120	3.0	0.0	50.4	1.3	41.2	95.9

Brennecke (1986) investigated the degradation and distribution of bitertanol in soil after seed treatment of spring wheat with the phenyl- and triazole-labelled compound at 75 g ai/100 kg seed (metabolism in wheat was also studied). The recovered radioactivity at the different sampling times

ranged from 12.1 to 41.5% in the 0-5 cm soil layer and from 0.2 to 2.3% in the 5-10 cm layer. The total radioactive residue at harvest amounted to 0.13 mg/kg as bitertanol in the top soil layer for the phenyl label and 0.2 mg/kg for the triazole label. The radioactive residue in the organic soil extracts consisted almost exclusively of unchanged bitertanol.

Brennecke (1982a) studied the aerobic degradation of [U-*phenyl*-^{14}C]bitertanol in loamy sand and sandy loam after application of an exaggerated rate corresponding to about 15 kg ai/ha. The study was conducted at 22°C and at 9°C, and samples were taken up to 92 days at the higher temperature and up to 180 days at the lower temperature.

Bitertanol was rapidly degraded at 22°C, with half-lives of 17 days in the loamy sand and 30 days in the sandy loam. At 9°C the half-life in the loamy sand was 70 days, in the sandy loam 179 days. $^{14}CO_2$ was the main product. The results are shown in Table 17.

Table 17. Results of aerobic incubation of [U-*phenyl*-^{14}C]bitertanol with two soils (Brennecke, 1982a).

	Sandy loam		Loamy sand	
Temperature, °C	9	22	9	22
Days after application	180	92	180	92
Recovery , %	101.8	98.1	94.9	92.8
$^{14}CO_2$, % of recovered ^{14}C	19.4	49.1	53.0	68.0
Unextracted, % of recovered ^{14}C	27.7	38.5	29.6	24.4

In only one of the five experiments (loamy sand, 22°C) bitertanol benzoic acid (BUE 2684) was found as an intermediate in the formation $^{14}CO_2$ in amounts between about 6 and 19%. An unknown product was also observed in amounts of $\leq$1%. These compounds were found at 7, 14 and 30 days, but not thereafter. In repeat experiments at 22°C and 9°C, no accumulation of the two compounds was observed; together they accounted for less than 2% of the ^{14}C. Neither compound was detected in the sandy loam soil, but an additional product was identified at both temperatures as the keto analogue of the parent compound (BUE 1662) at levels of 0.7 to 1.7%. It was not found in the loamy sand.

Puhl and Hurley (1979b) studied the aerobic soil degradation of [U-*phenyl*-^{14}C]bitertanol after application of 1.5 and 15 kg ai/ha to silt loam. The results corroborated those of Brennecke (1982a). Bitertanol was degraded in silt loam with a half-life of 14 days at the simulated field use rate of 1.5 kg/ha. The half-life at the exaggerated rate of 15 kg ai/ha was 20 days.

After incubation of the low-dose samples for 121 days, 8.4% of the applied radioactivity was organosoluble, the main constituent being bitertanol (6% of the applied ^{14}C); 0.8% was water-soluble, 45.0% was unextracted and 45.8% was evolved as $^{14}CO_2$ (Table 18). No other compounds were identified, whereas at the higher dose the two diastereoisomers of bitertanol benzoic acid (BUE 2684) were formed. Fractionation of the soil organic matter after 121 days showed that the previously unextracted radioactivity was distributed rather evenly in the humic acid, fulvic acid, and humin fractions at levels of 12.4%, 12.8 and 19.8% respectively.

An interesting difference between the 1.5 and 15 kg ai/ha samples was the presence of significant amounts of water-soluble radioactivity after 14 and 29 days in the high-dose samples. After acidification and extraction most of this radioactivity was identified as being due to bitertanol benzoic acid (BUE 2684).

Table 18. Distribution of radioactivity as % of that applied after aerobic incubation of [U-*phenyl*-^{14}C]bitertanol with silt loam (Puhl and Hurley, 1979b).

Period, days	Bitertanol	$^{14}CO_2$	Bitertanol benzoic acid	Not identified	Unextracted
	1.5 kg ai/ha				
0	98.6	---	---	1.2	0.2
3	90.7	0.8	---	3.9	4.6
7	67.8	7.1	---	4.6	20.5
14	46.8	15.4	---	6.6	31.2
30	22.9	29.7	---	4.8	42.6
59	12.7	40.8	---	4.1	42.4
91	8.5	42.8	---	2.8	45.9
121	6.0	45.8	---	3.2	45.0
	15 kg ai/ha				
0	98.3	---	---	1.6	0.1
7	86.4	2.3	---	4.0	7.3
14	61.0	12.0	6.5	4.0	16.5
29	28.7	25.8	8.6	5.4	31.5

Degradation under anaerobic conditions was also investigated and found to be slower (Table 19). Bitertanol was stable in sterilized soil.

Table 19. Comparative distribution of radioactivity in soil samples incubated with [U-*phenyl*-^{14}C]bitertanol under aerobic and anaerobic conditions (Puhl and Hurley, 1979b).

Conditions	Days	^{14}C, % of applied			
		Bitertanol	$^{14}CO_2$	Not identified	Unextracted
aerobic	30	22.9	29.7	4.8	42.6
	59	12.7	40.8	4.1	42.4
	91	8.5	42.8	2.8	45.9
anaerobic	28	20.8	33.0	6.2	40.0
	60	19.5	30.5	5.4	44.6

Takase and Yoshimoto (1980) studied the degradation of bitertanol in upland soil under laboratory and field conditions in Japan. In the laboratory the degradation half-life was 12 days in alluvial soil and 30 days in volcanic ash. In the field, bitertanol was applied 4 times at intervals of 7 or 10 days to peanut fields of the same soils at 500 g ai/ha. The computed half-lives were 14.6 days in the alluvial soil and 2.5 days in the volcanic ash, demonstrating the rapid degradation of bitertanol in soil.

ENVIRONMENTAL FATE IN WATER/SEDIMENT SYSTEMS

Hydrolysis

Wilmes (1981) investigated the hydrolysis of bitertanol. Degradation was only observed in the presence of Fe^{3+}. In an aqueous solution containing 50 mg/l bitertanol, 1% $FeCl_3$ and 20% ethanol to facilitate dissolution of the compound, the half-life was approximately 6 weeks at 70°C. No hydrolytic degradation was observed in distilled water, buffered solutions (pH 3-10) or 1% solutions of $CuCl_2$, $NaHCO_3$ or $CaCl_2$.

Nichols and Thornton (1979) investigated hydrolysis in sterile aqueous buffer solutions at pH 4, 7, and 9 maintained at 25°C and 40°C at concentrations of 0.25 and 2.5 mg/l. No degradation was apparent after 30 days. Recoveries ranged from 85 to 108%. The ratio of the isomers remained ttconstant and temperature had no noticeable effect. Bitertanol was evidently stable under the test conditions.

Photolysis in water

Hellpointner (1991) determined the quantum yield of the direct photodegradation of bitertanol in water in polychromatic light. From UV absorption data and the kinetic results of two photodegradation experiments in a carousel irradiation reactor the quantum yield was calculated to be 0.0697, and the half-life of direct photodegradation was calculated by two different simulation models to range from one month to one year for the periods of main use, indicating that direct photodegradation in water contributes little to the overall elimination of bitertanol in the environment.

Sietsema (1983) irradiated aqueous solutions of [*triazole*-^{14}C]bitertanol in a carousel device with an Ace photoreactor. The half-life was 37.7 to 52.2 h under these conditions, which could be extrapolated to about 11 days for the half-life of bitertanol under natural sunlight. The major photolysis products identified were 1,2,4-triazole, 4-hydroxybiphenyl, and a high molecular weight polymer. Several minor products, each accounting for << 10% of the total radioactivity, were also observed. The isomeric form I of bitertanol was photolysed slightly faster than form II.

Wilmes (1980, 1981) irradiated bitertanol dissolved in a mixture of acetonitrile and water (1:1). The initial degradation half-life was 1.2 hours with or without the addition of 2% acetone as a sensitiser. Several batches of technical grade bitertanol were examined under these conditions, with resulting half-lives of 2.2 to 2.8 h. A large number of degradation products were formed at low concentrations, 1,2,4-triazole and 4-hydoxybiphenyl being major components.

As a conclusion, bitertanol can be readily degraded by light but such degradation is likely to be reduced under environmental conditions since very little light of effective wavelengths (<290 nm) is available in water.

Aquatic degradation

Fritz (1990) investigated the degradation of [U-*phenyl*-^{14}C]bitertanol in two aquatic micro-ecosystems containing sediment. The samples originated from a recultivated gravel pit away from agricultural areas in Lienden (oligotrophic) and a drainage ditch in a fruit orchard in Ijzendoorn (eutrophic). The test compound was added to the water at a concentration of 1.0 mg/l which corresponded to an application rate of 1 kg ai/ha, assuming a water depth of 10 cm. The incubation was conducted at 22°C in the dark and lasted for 120 days.

A high proportion of the applied radioactivity was taken up by the sediment, reaching a maximum of 69 to 91% after 25 days. At the end of the test period of 120 days the total amount of radioactivity in the sediment had decreased to about 38 to 44% (Table 20). The unextractable radioactivity in the sediment of both systems amounted to about 35% on average after 120 days.

Table 20. Distribution of radioactivity as % of that applied in water/sediment after addition of [U-*phenyl*-^{14}C]bitertanol (Fritz, 1990).

Incubation, time	$^{14}CO_2$		Surface water incl. dissolved $^{14}CO_2$		Sediment		Total ^{14}C	
	Lienden	Ijzendoorn	Lienden	Ijzendoorn	Lienden	Ijzendoorn	Lienden	Ijzendoorn
2-3 hours	---	---	38.5	32.5	61.4	71.5	99.9	104.0
7 days	0.3	0.1	37.2	12.6	55.9	80.3	93.4	93.0
25 days	1.8	0.6	24.9	7.4	68.9	90.8	95.6	98.8
53 days	11.3	3.1	23.8	6.9	59.5	87.2	94.6	97.2
82 days	36.2	37.0	9.9	3.1	43.4	52.5	89.5	92.6
120 days	47.3	46.2	5.6	1.8	38.4	43.5	91.3	91.5

Bitertanol was rapidly degraded. Only about 2 to 3% of the parent compound was detected in the surface water of both systems after 53 days and was no longer detectable in the water phase after 82 days. The isomeric ratio was not affected. The sediment contained 24 to 59% of the applied

bitertanol after 53 days. This decreased to 3 to 4% at the end of the test period of 120 days. The degradation half-life of bitertanol in both waters varied between 24 and 27 days. Small amounts (≤1%) of bitertanol benzoic acid were detected in the surface water, and traces (0.4-0.8%) of the keto analogue (BUE 1662) in the sediment. Mineralization was extensive: after 120 days nearly half of the applied radioactivity was detected as $^{14}CO_2$. Bitertanol did not accumulate in the sediment. The results are shown in Table 21 and the degradation pathways in Figure 6.

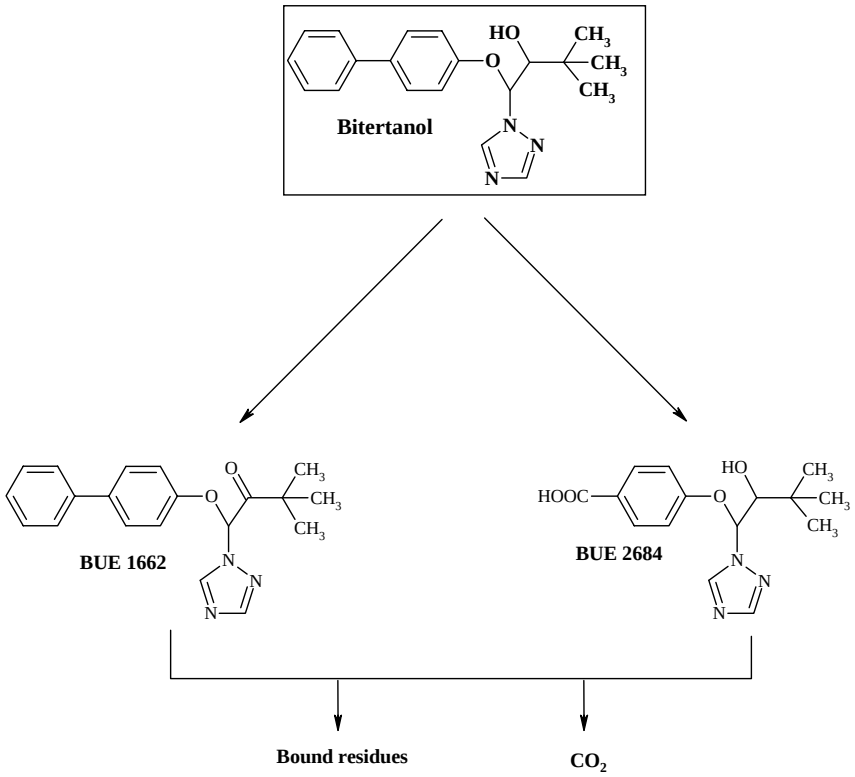
Table 21. Distribution of [U-*phenyl*-^{14}C]bitertanol and its degradation products in water/sediment systems as a function of the incubation period (Fritz, 1990).

Incubation period, days	^{14}C, % of applied											
	Total ^{14}C in water or extracted from sediment		Bitertanol		Bitertanol benzoic acid BUE 2684		Keto analogue BUE 1662		$^{14}CO_2$ [1]		Not identified	
	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.	Liend.	Ijzen.
	Surface water											
0	38.5	32.5	37.4	31.3	n.d.[1]	n.d.	n.d.	n.d.	---	---	1.1	1.2
7	37.2	12.6	35.4	11.8	< 01	0.2	n.d.	n.d.	0.6	0.2	1.5	0.8
25	24.9	7.4	16.4	4.1	0.5	0.5	n.d.	n.d.	2.1	0.8	8.1	3.0
53	23.8	6.9	2.9	1.6	n.d.	1.0	< 0.1	< 0.1	22.8	4.3	9.8	3.9
82	9.9	3.1	n.d.	n.d.	0.3	0.2	n.d.	n.d.	39.7	37.8	6.3	2.3
120	5.6	1.8	n.d.	n.d.	n.d.	n.d.	n.d.	n.d.	48.9	46.7	4.0	1.3
	Sediment											
0	55.0	59.4	53.3	57.2	n.d.	n.d.	n.d.	n.d.	---	---	1.7	2.2
7	48.5	69.3	46.5	66.7	n.d.	n.d.	n.d.	n.d.	0.3	0.2	2.0	2.6
25	57.0	75.6	53.9	71.9	n.d.	n.d.	n.d.	0.4	0.4	0.5	3.1	3.3
53	26.8	63.5	23.5	58.8	n.d.	n.d.	0.4	0.8	0.6	0.3	2.9	3.9
82	12.6	12.5	10.3	10.2	n.d.	n.d.	0.1	0.2	0.2	0.2	2.2	2.1
120	5.3	6.1	3.2	4.0	n.d.	n.d.	< 0.1	0.1	0.1	0.1	2.1	2.0

n.d. not detected

[1] [1] $^{14}CO_2$ in surface water includes that in the CO_2 trap

Figure 6. Proposed pathways of bitertanol degradation in water/sediment systems (Fritz, 1990).



METHODS OF RESIDUE ANALYSIS

Regulatory analytical methods

DFG method S 19 was validated for bitertanol in plant materials (Specht and Thier, 1989). Recoveries were 80-100% and the limit of determination (LOD) was 0.5 mg/kg. DFG method 613 was validated for bitertanol in plant materials, soil and water by Brennecke (1987). Recoveries were between 82 and 114%. Limits of determination were 0.01-0.05 mg/kg for plant materials, 0.05 mg/kg for soil and 0.005 mg/l for water.

A multi-residue method for non-fatty and fatty foods was provided by the government of The Netherlands (Olthof, 1999a). The residues are extracted with acetone/water or ethyl acetate. There is no clean-up for plant materials but animal products are cleaned up by gel-permeation chromatography (GPC), HPLC or liquid-liquid partitioning (LLP). Determination is by gas chromatography with an ion trap detector (ITD) or nitrogen-phosphorus detector (NPD). The LOD was reported as 0.05 mg/kg for both non-fatty and fatty foods and recoveries were generally between 90 and 100%.

DFG multi-residue method W 5 was applied to bitertanol in water (Brennecke and Vogeler, 1987) with recoveries between 91 and 114%. The LOD was 0.005 mg/l. A thin-layer separation with UV detection and automated multiple development (Burger, 1988) was applied to bitertanol in ground and drinking water with recoveries between 85 and 116%. The LOD was 0.05 µg/l.

Animal materials have been analysed by gas chromatography with an NPD after clean-up by gel-permeation chromatography and mini-silica gel column chromatography (Specht and Tillkes, 1980a). An enforcement method for the determination of bitertanol residues in bovine and poultry tissues, milk and eggs (Sandie and Coffman, 1985) was based on gas chromatography with nitrogen-specific detection (NPD). Samples were extracted with acetone and methylene chloride and cleaned up by various procedures. Recoveries ranged from 79 to 103% for tissues (0.5 mg/kg fortification), 87

to 89% for milk (0.1 mg/kg fortification), and 66% at 0.01 mg/kg to 104% at 0.05 mg/kg for eggs. The lowest fortification levels were 0.5, 0.1 and 0.01 mg/kg respectively.

Specialized methods

The following specialized methods were used for the analysis of the plant and animal samples in the supervised trials.

Thornton, 1977 (method F 107). This method was applied to the determination of bitertanol in apples. Samples were macerated in acetone and the filtered raw extract partitioned with dichloromethane. The dichloromethane phase was purified by column chromatography on Florisil. The analyte was determined by gas chromatography with a phosphorus/nitrogen selective flame ionization detector. Recoveries were between 86 and 108% at fortification levels of 0.05 and 0.5 mg/kg. The LOD was 0.05 mg/kg.

The method was also validated for bananas. Recoveries from banana peel and pulp ranged from 56 to 85% at a fortification level of 0.05 mg/kg, and from 86 to 114% at 0.1 mg/kg (Becker, 1980). Further determinations of recoveries from the pulp and peel of green and ripe bananas at a fortification level of 0.05 mg/kg gave recoveries of 82 to 90% from green and 70 to 88% from ripe bananas. Ripe peel was also fortified at incremental rates from 0.02 to 0.1 mg/kg, giving recoveries of 100 to 120% (Disher, 1982). The LOD for all banana commodities was 0.01 mg/kg.

Specht and Tilkes, 1980b (method 00029, formerly F 136). This method was developed for the determination of bitertanol in plant materials. After extraction with acetone and liquid-liquid partitioning with dichloromethane the organic phase is purified by gel-permeation chromatography and the analyte determined by GLC with an NPD. Recoveries were between 74 and 112% at fortification levels between 0.02 and 2.4 mg/kg. The LOD was 0.02 mg/kg.

The method was modified by including a silica gel clean-up before, or in bananas and peaches after, gel-permeation chromatography (Specht and Tilkes, 1982 [modification M003], 1981a,b, modification M004/006). It was validated with several plant materials with recoveries between 80 and 107% at fortification levels between 0.01 and 5.0 mg/kg. The LOD was 0.05 mg/kg. A further modification gave an LOD of 0.01 mg/kg for banana fruit and peel (Brennecke, 1983b, modification M003/E013).

Another modification with changes to sample weights and details of the gel-permeation chromatography (Brennecke, 1981a, modification M009) gave a recovery of 97% from peaches at 0.05 mg/kg.

For black currants and beans the clean-up had to be further improved (Brennecke, 1981a, modification M009). Interferences were removed by acetonitrile/n-hexane partition, acetonitrile/water/dichloromethane partition and column chromatography on silica gel as well as gel-permeation chromatography. Recoveries were between 93 and 110% at fortification levels between 0.05 and 0.5 mg/kg. The LOD was 0.05 mg/kg.

Recovery data for several crops are reported in the following supplements to method 00029: E001 - barley (Brennecke, 1983c), E002 - cucumbers (Brennecke, 1981b), E003 – oat forage (Brennecke, 1982b), E005 – oat grain and straw (Brennecke, 1982c), E006 - peaches and gooseberries (Brennecke, 1982d), E007 – rye forage (Brennecke, 1983d), E008- rye grain and straw (Brennecke, 1982e).

Brennecke, 1985 (method 000031, formerly F223). Bitertanol is extracted from plant material with acetone for samples with high water content and with an acetone/water mixture for samples with low water content. Clean-up is by column chromatography on silica gel and gel-permeation chromatography on Bio Beads S-X 3 polystyrene gel, and determination by gas chromatography with

a nitrogen-specific thermionic dectector. Recoveries ranged from 80 to 105% and LODs from 0.01 to 0.05 mg/kg. In supplement E003 the method was validated for nectarines (Möllhoff, 1986), and in E006 for tea (Brennecke, 1995).

Brennecke, 1988a,b (method 00003, formerly F281, modification M002). Sample from plants and their processed commodities are extracted with acetone (acetone/water for dry materials) and the filtered extracts applied to a disposable extraction column after evaporation of the acetone. Bitertanol is eluted with a mixture of cyclohexane and ethyl acetate and determined by HPLC with fluorescence detection. Recoveries over a range of 0.002 to 20 mg/kg were between 65 and 105%. The LOD was 0.02 mg/kg for raw and processed plant commodities and 0.002 mg/kg for beverages.

In modifications M004 and M006 (Bachmann, 1994a,b) and M006/E003 (Nüßlein, 1995) the aliquot is taken from the filtered raw extract instead from the aqueous phase after evaporation of the acetone. Extracts of bananas and peach juice are removed from the macerate by suction instead of filtration. Recoveries were between 79 and 100% at fortification levels between 0.01 and 1 mg/kg. The LOD was 0.01 mg/kg for banana fruit and peel and peach juice, and 0.02 mg/kg for peach fruit.

Method 00003 was also validated for cherry jam (modification E001, Köhler, 1989) and tomato preserve, paste and juice (modification E002, Krebber, 1991).

Allmendinger, 1998 (modification of method 00462). An LC-MS-MS method was developed for the determination of bitertanol and fuberidazole in wheat forage, grain and straw. The purpose of the modification was to extend the method to new sample materials which required an additional clean-up (extraction on Chem-Elut). The mean recoveries of bitertanol were 80 to 99%. The LOD was 0.05 mg/kg.

Leimkuehler *et al.*, 1983 (method F218). The method was developed to quantify bitertanol and its metabolites in bovine tissues, milk, poultry tissues and eggs. Samples are extracted with acetone, methanol or hexane and hydrolysed with acid to release 1,2,4-triazole. The triazole is converted to triazolylpinacolone which is determined by gas chromatography with an NPD. Several clean-up steps are required including partitioning, ion-exchange chromatography and high-performance liquid chromatography. Recoveries, determined at 0.05 and 0.1 mg/kg with all samples and also at 0.5 and 2.0 mg/kg with bovine liver, were between 60 and 120%. The LOD was 0.01 mg/kg.

Stability of residues in stored analytical samples

Plant materials

The storage stability of bitertanol on dry beans, green beans, apples, peaches and cherries was determined (Mobay Chemical Corporation, 1983a,b, 1984a,b; Köhler, 1993). Samples were spiked with bitertanol at 0.1 and 1.0 mg/kg (dry beans), 0.2 mg/kg (cherries), and 0.5 mg/kg (green beans). The stability of incurred residues was determined in apples and peaches. Frozen samples were stored at temperatures below -20°C.

Bitertanol was stable (recoveries 85-87%) in green beans, apples and peaches for at least as long as the study lasted, 406, 1262 and 797 days respectively. Recoveries from dry beans were $\geq$80% for 10-12 months but only 50-60% after 14 or 15.5 months. (In the residue trials on plants with a low water content, cereal grains and bananas, no samples were stored for more than a year). The recovery from cherries was generally >70%, and $\geq$80% of the recovery from concurrent analyses of freshly fortified samples, showing that residues of bitertanol were stable in cherries for the tested times of storage.

In summary, bitertanol residues were found to be stable in green and dry beans for more than 1 year, in peaches and cherries for at least 2 years, and in apples for at least 3.5 years. The results are shown in Table 22.

Table 22. Storage stability of bitertanol in plant commodities.

Sample	Fortification, mg/kg	Storage period, days	Recovery, %		Reference Report no.
Dry beans	0.1	0	100		Mobay, 1983a 84252
		255	80		
		314	80		
		416	60		
	1.0	0	100		
		48	95		
		303	89		
		362	100		
		464	54		
Green beans	0.5	0	-		Mobay, 1984a 84571
		61	91		
		151	88		
		406	87		
Apples	-	0	100		Mobay, 1984b 84264
		1262	85		
Peaches	-	0	100		Mobay, 1983b 84222
		797	87		
			% remaining	Concurrent recovery	
Cherries	0.2	0	94	101	Köhler, J., 1993 RA-212/93
		35	89	-	
		59	79	-	
		88	76	92	
		179	60	-	
		401	61	78	
		731	79	83	

Animal products

Leimkuehler (1983) determined the storage stability of radiolabelled bitertanol and *p*-hydroxybitertanol in the liver, kidneys, muscle and fat from the metabolism study on a dairy cow (Obrist *et al.*, 1983). The samples were held in cold storage (-18° to -23°C) for approximately 2 years. The results showed no significant loss of bitertanol or *p*-hydroxybitertanol residues in any of the four tissues over the two year period. The Meeting noted the very low level of the residues in kidneys, muscle and fat.

Table 23. Storage stability of residues in animal products.

Sample	Storage period, days	Recovery in stored sample		Reference Report no.
		Bitertanol	*p*-hydroxybitertanol	
Liver	0	0.056 mg/kg = 100 %	0.325 mg/kg = 100 %	Leimkuehler, 1983 84126
	825	89 %	110 %	
Kidneys	0	0.006 mg/kg = 100 %	0.021 mg/kg = 100 %	
	825	83 %	110 %	
Muscle	0	0.001 mg/kg = 100 %	0.004 mg/kg = 100 %	
	825	100 %	225 %	
Fat	0	0.008 mg/kg = 100 %	0.006 mg/kg = 100 %	
	825	150 %	233 %	

Definition of the residue

On the evidence of metabolism studies with foliar spray treatments of apples, cotton and peanuts, the residue of concern is bitertanol *per se*.

After seed treatment of wheat at a commercial application rate, the metabolites detected in the grain at harvest (from the triazole ring label) were conjugates of 1,2,4-triazole, triazolylalanine (50-66% of the total ^{14}C, 0.12-0.16 mg/kg) and triazolylacetic acid (22-34% of total ^{14}C, 0.04-0.07 mg/kg). The parent compound was not detectable in the grain. The presence of free 1,2,4-triazole was excluded by chromatographic comparison with the authentic reference compound.

As 1,2,4-triazolylalanine is a plant metabolite of several pesticides that contain a 1,2,4-triazole moiety, being formed by its conjugation with serine, the conjugate was evaluated by the 1989 JMPR for toxicology and residues. The 1989 Meeting concluded that residues of 1,2,4-triazolylalanine arising from the use of triazole fungicides do not present a toxicological hazard.

The metabolism studies on rats, a dairy cow and laying hens indicate that bitertanol and the metabolite *p*-hydroxybitertanol (free and conjugated) are the main residue components in animal tissues, milk and eggs.

As bitertanol has no acidic or basic properties in aqueous solution, the partition coefficient will not be influenced by the pH. The octanol-water partition coefficients (log P_{OW} = 4.04 diastereoisomer A, 4.15 diastereoisomer B) indicate that bitertanol is fat-soluble.

The Meeting concluded that the following residue definitions are appropriate.

For compliance with MRLs. For plant and animal products: bitertanol.

For estimations of dietary intake. For plant products: bitertanol. For animal products: sum of bitertanol, *p*-hydroxybitertanol and the acid-hydrolysable conjugates of *p*-hydroxybitertanol.

USE PATTERN

Information on GAP was received from the manufacturer and the governments of Australia, Germany, The Netherlands, Poland and the UK. The major registered uses of bitertanol on food crops are shown in Tables 24 (foliar spray) and 25 (seed treatment).

Table 24. Registered uses of bitertanol as foliar sprays or pruning paint.

Crop	Country	Form.	F/G	Application				PHI, days
				Method	Rate [kg ai/ha]	Spray conc. [kg ai/hl]	No.	
Apple	Austria	25 WP	F	Foliar spray	0.19-0.25	0.013-0.017	2-3	21
	Australia	10 LA[1]	F	Pruning paint	undiluted			14
	Belgium	25 WP	F	Foliar spray	0.19-0.38	0.013-0.025		42
		500 SC	F	Foliar Spray	0.19-0.38	0.013-0.025		42
	France	25 WP	F	Foliar spray		0.019-0.025		14
	Germany	25 WP	F	Foliar spray	0.19	0.013	1-5	14
	Greece	25 WP	F	Foliar spray	0.25-0.5	0.013-0.025		14
	Italy	25 WP	F	Foliar spray	0.23-0.3	0.019-0.025		21
	Netherlands	25 WP	F	Foliar spray	0.2-0.34	0.02	2-5	14
	Poland	25 WP	F	Foliar spray	0.29-0.38	0.029-0.08	2-3	14
		72.5 WP[2]	F	Foliar spray	0.28	0.03-0.06		14
	Portugal	500 SC	F	Foliar spray	0.19	0.019		21
	South Africa	68.75 WP[3]	F	Foliar spray	0.09-0.26	0.008	1-2	14
	Spain	25 WP	F	Foliar spray	0.25-0.38	0.025-0.038		15
	Switzerland	55 WP[4]	F	Foliar spray	0.2-0.25	0.01 – 0.015	1-4	21
	Turkey	25 WP	F	Foliar spray	0.25	0.013		14

Crop	Country	Form.	F/G	Application				PHI, days
				Method	Rate [kg ai/ha]	Spray conc. [kg ai/hl]	No.	
Banana	Cameroon	300 EC	F	Foliar spray	0.15	1.5-3		
	Belize	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Costa Rica	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Dominican Republic	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Guatemala	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Honduras	300 EC	F	Foliar spray	0.15	0.02-0.2		0
	Nicaragua	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Panama	300 EC	F	Foliar spray	0.15	0.5-1.4		0
	Philippines	300 EC	F	Foliar spray via air plane	0.15-0.20	0.5-0.65		0
	Taiwan	300 EC	F	Foliar spray	0.12	0.4		6
Barley, winter	Germany	25 WP	F	Foliar spray	0.375	0.094	1	NS[5]
Beans	Australia	300 EC	F	Foliar spray	0.15		3	3
Cherries	Austria	25 WP	F	Foliar spray	0.56	0.038	1-2	A[6]
	Belgium	25 WP	F	Foliar spray	0.56	0.038	2-3	A
		500 SC	F	Foliar spray	0.56	0.038	2-3	A
	Germany	25 WP	F	Foliar spray	0.56	0.038	3	21
	Greece	25 WP	F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Netherlands	25 WP	F	Foliar spray	0.19	0.013	2-3	21
	Poland	25 WP	F	Foliar spray	0.38	0.038-0.08	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	14
	Switzerland	55 WP[4]	F	Foliar spray	0.2	0.01		21
Courgette	Netherlands	500 EC	G	Foliar spray	0.15- 0.45 or 0.9	0.03	3-9	3
Cucumber	Belgium	300 EC	G	Foliar spray	0.6	0.03		3
		500 SC	G	Foliar spray	0.6	0.03		3
	Italy	25 WP	G	Foliar spray	0.19-0.22	0.019-0.025	2-3	14
	Netherlands	300 EC 500 EC	G	Foliar spray	0.15-0.45 or 0.9	0.03	3-9	3
Melons	Netherlands	300 EC 500 EC	G[7]	Foliar spray	0.15- 0.45 or 0.9	0.03	3-9	3
Nectarine	France	300 EC	F	Foliar spray		0.03	usp[7]	14
		25 WP	F	Foliar spray		0.019-0.025		14
	Greece	25 WP	F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	7
	South Africa	300 EC	F	Foliar spray	0.14-0.36	0.012		35
	Spain	25 WP	F	Foliar spray	0.38-0.56	0.025-0.038	1-3	15
Peach	France	25 WP	F	Foliar spray		0.019-0.025		14
		300 EC	F	Foliar spray		0.03	usp[7]	14
	Greece	25 WP	F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	7
	South Africa	300 EC	F	Foliar spray	0.14-0.36	0.012		35
	Spain	25 WP	F	Foliar spray	0.38-0.56	0.025-0.038	1-3	15
Pear	Austria	25 WP	F	Foliar spray	0.19-0.25	0.013-0.0175	2-3	21
	Belgium	25 WP	F	Foliar spray	0.19-0.38	0.013-0.025		42
		500 SC	F	Foliar spray	0.19-0.38	0.019-0.025		42
	France	25 WP	F	Foliar spray		0.013-0.025		14
	Germany	25 WP	F	Foliar spray	0.19	0.013	1-5	14
	Greece	25 WP	F	Foliar spray	0.25-0.5	0.013-0.025		14
	Italy	25 WP	F	Foliar spray	0.23-0.3	0.019-0.025		21
	Netherlands	25 WP	F	Foliar spray	0.2-0.3	0.02	2-5	14
	Poland	72.5 WP[2]	F	Foliar spray	0.28	0.03-0.06	2-3	14
	Portugal	500 SC	F	Foliar spray	0.19	0.019		21
	South Africa	68.75 WP[3]	F	Foliar spray	0.09-0.26	0.008	1-2	14
	Spain	25 WP	F	Foliar Spray	0.25-0.38	0.025-0.038		15
	Switzerland	55 WP[4]	F	Foliar spray	0.2-0.25	0.01-0.015	1-4	21
	Turkey	25 WP	F	Foliar spray	0.25	0.013		14

Crop	Country	Form.	F/G	Application				PHI, days
				Method	Rate [kg ai/ha]	Spray conc. [kg ai/hl]	No.	
Pepper, sweet	Netherlands	500 EC	G	Foliar spray	0.15-0.45 or 0.9	0.03	3-9	3
Plums	Belgium	25 WP	F	Foliar spray	0.56	0.038	2-3	A
		500 SC	F	Foliar spray	0.56	0.038	2-3	A
	France	25 WP	F	Foliar spray		0.019-0.025		14
		300 EC	F	Foliar spray		0.03	nsp[7]	14
	Greece		F	Foliar spray	0.5-0.75	0.025-0.038		10
	Italy	25 WP	F	Foliar spray	0.38-0.45	0.025-0.03	2-3	21
	Poland	25 WP	F	Foliar spray	0.38	0.038-0.08	2-3	21
	Portugal	500 SC	F	Foliar spray	0.25-0.3	0.017-0.02	1-2	7
	Switzerland	55 WP[2]	f	Foliar spray	0.2	0.01		21
Tomato	Belgium	300 EC	G	Foliar spray	0.6	0.03		3
		500 SC	G	Foliar spray	0.6	0.03		3
	Netherlands	500 EC	G	Foliar spray	0.15-0.45 or 0.9	0.03	3-9	3

[1]10 LA :10 g/l bitertanol + 10 g/l 8-hydroxyquinoline sulfate
[2]72.5WP :12.5 % bitertanol + 60 % captan
[3]68.75 WP: in-can mixture: 7.5 % bitertanol + 60% captan + 1.25 % triadimenol
[4]55 WP : in-can mixture: 5 % bitertanol + 50% captan
[5]NS : PHI controlled by stage of growth at time of application. PHI in days not stated
[6]A : not applicable, as treatments during the growth stage of flowering only are registered
[7]nsp : number of treatments not specified. Label: use at the blossom and during the season, avoid repeated applications.
F : field; G: greenhouse

Table 25. Registered uses of bitertanol for seed treatment.

Crop	Country	Form.	Bitertanol content	kg ai/100 kg seed
Field pea	Poland	FS	33.8%	0.08
Lupin	Poland	FS	33.8%	0.08
Barley	France	FS	75 g/l	0.015
	Netherlands	DS	37.5%	0.056
	Sweden	LS	280 g/l	0.07
	UK	FS	188 g/l	0.038
Oats	Austria	FS	375 g/l	0.038-0.075
	France	FS	75 g/l	0.015
		FS	37.5 g/l	0.015
	Germany	FS	375 g/l	0.056
		DS	37.5%	0.056
		FS	190 g/l	0.057
	UK	FS	187.5 g/l	0.056
		FS	375 g/l	0.056
		LS	140 g/l	0.056
	Netherlands	DS	37.5%	0.056
	Poland	FS	33.8%	0.05
	Sweden	LS	280 g/l	0.056-0.07
Rye	Austria	FS	375 g/l	0.038-0.075
	Denmark	LS	280 g/l	0.028-0.042
	France	FS	37.5 g/l	0.015
	Germany	FS	375 g/l	0.056
		DS	37.5%	0.056
		FS	190 g/l	0.057
	UK	FS	187.5 g/l	0.056
		FS	375 g/l	0.056
	Netherlands	DS	37.5%	0.056
	Poland	FS	33.8%	0.05

Crop	Country	Form.	Bitertanol content	kg ai/100 kg seed
	Sweden	LS	280 g/l	0.056
Triticale	Denmark	LS	280 g/l	0.028-0.042
	UK	FS	187.5 g/l	0.056
		FS	375 g/l	0.056
	Poland	FS	33.8%	0.07
Wheat	Austria	FS	375 g/l	0.038-0.075
	Belgium	FS	190 g/l	0.038
		FS	75 g/l	0.015
		FS	37.5 g/l	0.015
		DS	37.5%	0.038
	Denmark	LS	280 g/l	0.028-0.042
	France	FS	75 g/l	0.015
		FS	37.5 g/l	0.015
	Germany	FS	375 g/l	0.075
		DS	37.5%	0.075
		FS	190 g/l	0.076
	UK	FS	187.5 g/l	0.056
		LS	140 g/l	0.056
		FS	375 g/l	0.056
		LS	280 g/l	0.056
		FS	188 g/l	0.038
	Netherlands	DS	37.5%	0.056
	Poland	FS	33.8%	0.07
	Sweden	LS	280 g/l	0.056-0.07

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the residue trials are shown in Tables 26 to 33 (foliar sprays) and Tables 34 to 38 (seed treatments).

Table 26. Residues of bitertanol from supervised trials on apples and pears.
Table 27. Residues of bitertanol from supervised trials on cherries.
Table 28. Residues of bitertanol from supervised trials on plums.
Table 29. Residues of bitertanol from supervised trials on nectarines.
Table 30. Residues of bitertanol from supervised trials on peaches.
Table 31. Residues of bitertanol from supervised trials on bananas.
Table 32. Residues of bitertanol from supervised trials on greenhouse tomatoes.
Table 33. Residues of bitertanol from supervised trials on greenhouse cucumbers.
Table 34. Residues of bitertanol from supervised trials on spring barley (seed treatment).
Table 35. Residues of bitertanol from supervised trials on oats (seed treatment).
Table 36. Residues of bitertanol from supervised trials on rye (seed treatment).
Table 37. Residues of bitertanol from supervised trials on spring wheat (seed treatment).
Table 38. Residues of bitertanol from supervised trials on winter wheat (seed treatment).

Where residues were not detected they are recorded in the Tables as below the limit of determination (LOD). Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although all trials included control plots, no control residues are recorded in the Tables except where they exceeded the LOD. Results are not corrected for recovery.

Most trials were carried out in Europe. In view of the different European climatic conditions, the residue trials were evaluated according to the common practice of the European Community (EC, 1998), complying with the critical GAP of northern and/or southern Europe. For the evaluation of the residue trials the regions of equal climatic conditions were defined as follows.

Northern and Central Europe: Sweden, Norway, Denmark, the UK, Ireland, northern and central France, Belgium, The Netherlands, Germany and Poland.

Southern Europe and the Mediterranean: Spain, Portugal, southern France, Italy and Greece.

Foliar spray uses

Apples and pears. (Table 26). The use of bitertanol on pome fruit is widely registered throughout Europe and in South Africa.

Trials in northern Europe on apples and pears were carried out in Germany, with both high-volume and low-volume atomizing spraying. With a water rate of 1500 or 2000 l/ha the spray concentration was 0.019 or 0.025 kg ai/hl, and with a water rate of 300, 500 or 750 l/ha the concentration was 0.05, 0.06 or 0.09 kg ai/hl. The application rate related to area was 0.28, 0.38 or 0.5 kg ai/ha. The number of treatments was 8 in 7 trials, 10 in 3 trials, and 12 in 2 trials. The spraying intervals ranged from 7 to 14 days. Except for the first treatment in 4 trials, all treatments were after flowering.

Eight residue trials on apples in southern Europe were in Italy, Spain and southern France. The spray concentrations were either 0.025 or 0.038 kg ai/hl and the water volumes 800-1500 l/ha. Thus the bitertanol applied per hectare was 0.25-0.46 kg. There were 5 applications in all the trials. The treatments were carried out during the stages of (1) bud to leaf development, (2) emergence of inflorescence to flowering, (3) end of flowering, (4) fruit development (fruit about final size), and (5) early to advanced maturity of fruit. In all but one of the trials samples were collected after a pre-harvest interval of 14 days.

In 7 trials in South Africa, apple trees received 6 or 7 high-volume sprays (1800-3500 l/ha) at a concentration of 0.013 kg ai/hl, corresponding to 0.23-0.44 kg ai/ha. Two other trials were at 0.88 kg ai/ha. The spraying intervals were generally 9-14 days.

Table 26. Residues of bitertanol from supervised trials on apples and pears.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10340-82 Germany, 1982	Williams Christ pear	500 SC	0.19	375	0.0125	12		0	1.4
								7	1.3
								10	0.69
								14	1.1
								21	0.82
10306-82 Germany, 1982	Williams Christ pear	25 WP	0.19	375	0.0125	12		0	1.2
								7	0.81
								10	0.75
								14	0.91
								21	0.47
10307-82 Germany, 1982	Williams Christ pear	25 WP		250	0.0125	12		0	0.69
								7	0.28
								10	0.2
								14	0.2
								21	0.23
10310-82 Germany, 1982	Williams Christ pear	25 WP	0.19	375	0.0125	12		0	1.7
								7	1.2
								10	0.98
								14	0.97
								21	0.57

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10311-82 Germany, 1982	Williams Christ pear	25 WP		250	0.0125	12		0 7 10 14 21	0.63 0.42 0.34 0.25 0.25
10341-82 Germany, 1982	Williams Christ pear	500 SC		250	0.0125	12		0 7 10 14 21	0.98 0.55 0.28 0.3 0.33
10302-82 Germany, 1982	Williams Christ pear	25 WP	0.19	375	0.0125	12		0 7 10 14 21	1.4 1.2 1.5 0.92 0.85
10303-82 Germany, 1982	Fruehe aus Trevoux pear	25 WP	0.19	375	0.0125	12		0 7 10 14 21 28	1 0.5 0.43 0.62 0.57 0.43
10322-83 Germany, 1983	Fruehe aus Trevoux pear	500 SC	0.19	375	0.0125	12		0 7 10 14 21 28	1.32 1.63 0.98 0.59 0.53 0.65
10323-83 Germany, 1983	Williams Christ pear	500 SC	0.19	1500	0.0125	12		0 7 10 14 21	0.88 0.48 0.36 0.22 0.17
10301-86 Germany, 1986	Alexander Lucas pear	25 WP	0.19	1500	0.0125	12		0 7 10 14 21	1.2 1.1 1.2 0.93 0.62
10311-86 Germany, 1983	Alexader Lucas pear	500 SC	0.19	1500	0.0125	12		0 7 10 14 21	1 1.1 0.89 0.92 0.45
10300-78 Germany, 1978	Jonathan apple	25 WP	0.5	2000	0.0125	10	fruit diameter 62 mm	0 4 14 21	1.0 0.92 0.69 <u>0.70</u>
10301-78 Germany, 1978	Cox Orange apple	25 WP	0.5	2000	0.025	10	fruit diameter 63 mm	0 4 7 14 21	1.2 1.2 0.64 0.66 <u>0.86</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10303-78 Germany, 1978	James Grieve apple	25 WP	0.5	2000	0.025	8	fruit diameter 67 mm	0 4 7 14 21	1.1 0.85 1.2 0.62 0.61
10305-79 Germany, 1979	Golden Delicious apple	25 WP	0.38	1500	0.025	10	87	0 7 10 14 21	1.5 1.8 1.7 1.8 1.0
10313-80 Germany, 1980	Jonathan apple	25 WP	0.38	750 (1500)[1]	0.05 (0.025)[1]	12	fruit diameter 60 mm	0 7 10 14 21	0.27 0.19 0.15 0.13 0.12
10304-83 Germany, 1983	Golden Delicious apple	25 WP	0.28	500 (1500)	0.06 (0.02)	12	8 weeks before harvest	0 7 14 21 28	0.63 0.42 0.25 0.2 0.16
10300-84 Germany, 1984	James Grieve apple	25 WP	0.28	1500	0.019	8	fruit diameter 56 mm	0 7 10 14 21	0.55 0.6 0.3 0.55 0.3
10301-84 Germany, 1984	Jonathan apple	25 WP	0.28	1500	0.019	8	fruit diameter 59 mm	0 7 10 14 21	0.4 0.2 0.1 0.08 0.05
10302-84 Germany, 1984	James Grieve apple	25 WP	0.28	300 (1500)	0.09 (0.018)	8	85	0 7 10 14 21	1 0.6 0.6 0.23 0.2
10303-84 Germany, 1984	Golden Delicious apple	25 WP	0.28	300 (1500)	0.09 (0.018)	8	85	0 7 10 14 21	1.1 0.8 0.7 1.0 0.8
10304-84 Germany, 1984	James Grieve apple	25 WP	0.28	1500	0.019	8	fruit diameter 52 mm	0 7 10 14 21	0.2 0.1 0.09 0.09 0.05
10305-84 Germany, 1984	James Grieve apple	25 WP	0.28	1500	0.019	8	fruit diameter 52 mm	0 7 10 14 21	0.16 0.12 0.09 0.13 0.07

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RA-2010/93 303267 Italy, 1993	Perleberg apple	25 WP	0.38	1500	0.025	5	81	0 3 7 10 14 21	0.24 0.18 0.19 0.14 <u>0.24</u> 0.07
RA-2010/93 303283 Spain, 1993	Golden apple	25 WP	0.30 0.33 0.38	800 890 1000	0.038 0.038 0.038	1 1 3	81	0 21	0.62 0.23
RA-2010/93 303291 Spain, 1993	Golden apple	25 WP	0.37 0.44 0.46	987 1174 1227	0.038 0.038 0.038	1 3 1	81	0 3 6 11 14 21	0.37 0.48 0.49 0.31 <u>0.36</u> 0.36
RA-2104/96 606944 Spain, 1996	Starking apple	500 SC	0.25 0.33 0.38	1000 1300 1500	0.025 0.025 0.025	3 1 1	85	0 3 7 10 14 21	0.22 0.24 0.21 0.24 0.15 <u>0.18</u>
RA-2104/96 606960 Spain, 1996	Golden apple	500 SC	0.25 0.33 0.38	1000 1300 1500	0.025 0.025 0.025	3 1 1	85	0 3 7 10 14 21	0.37 0.32 0.35 0.26 <u>0.34</u> 0.19
RA-2104/96 606979 Italy, 1996	Granny Smith apple	500 SC	0.26 0.24 0.34 0.36 0.37	1020 977 1455 1450 1480	0.025 0.025 0.023 0.025 0.025	1 1 1 1 1	79	0 14 21	0.29 <u>0.09</u> 0.06
RA-2104/96 606987 Italy, 1996	Red Chief apple	500 SC	0.24 0.25 0.38 0.38 0.36	952 1002 1536 1532 1437	0.025 0.025 0.025 0.025 0.025	1 1 1 1 1	79	0 14 21	0.22 <u>0.08</u> 0.05
RA-2104/96 606995 South France, 1996	Golden Delicious apple	500 SC	0.25 0.38	1000 1500	0.025 0.025	3 2	85	0 14 21	0.31 <u>0.23</u> 0.19
311/88195/V 144 South Africa, 1981	Star Crimson apple	25 WP	0.23	1800	0.013	7	--	0 7 14 22 29 36	1.1 0.68 0.66 0.36 0.31 0.18

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treatments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
311/88161/V 16A South Africa, 1981	Starking apple	25 WP	0.38	3000	0.013	7	--	0	0.83
								9	0.77
								19	0.36
								26	0.50
								34	0.46
								42	0.23
311/88161/V 16B South Africa, 1981	Golden Delicious apple	25 WP	0.38	3000	0.013	7	--	0	1.0
								9	0.55
								19	0.25
								26	0.26
								34	0.36
								42	<0.05
311/88352/W 26A South Africa, 1982	Golden Delicious apple	25 WP	0.88	3500	0.025	7	--	0	1.6
								5	0.88
								13	0.58
								19	1.1
								27	0.36
								34	0.24
311/88352/W 26B South Africa, 1982	Golden Delicious apple	25 WP	0.44	3500	0.013	7	--	0	1.9
								5	0.66
								13	0.50
								19	0.52
								27	0.26
								34	0.17
311/88352/W 26C South Africa, 1982	Golden Delicious apple	25 WP	0.44	3500	0.013	6	--	0	1.8
								8	0.92
								16	0.56
								22	0.54
								30	0.61
								37	0.44
								44	0.11
311/88352/W 29A South Africa, 1982	Starking apple	25 WP	0.875	3500	0.025	7	--	0	1.5
								5	1.2
								13	1.1
								19	0.51
								27	0.4
								34	0.34
311/88352/W 29B South Africa, 1982	Starking apple	25 WP	0.44	3500	0.013	7	--	0	0.75
								5	0.61
								13	0.71
								19	0.25
								27	0.27
								34	0.24
311/88352/W 29C South Africa, 1982	Star Crimson apple	25 WP	0.44	3500	0.013	6	--	0	1.8
								8	1.1
								16	0.45
								22	0.36
								30	0.31
								37	0.18
								44	0.16

[1]kg ai/hl calculated for 1500 l water/ha

Cherries (Table 27). The use of bitertanol on cherries is widely registered throughout Europe.

In Germany 14 residue trials on sour cherries were carried out with high- and low-volume spraying. The spray concentrations were 0.08, 0.15, or 0.19 kg ai/hl (low-volume atomizing spraying, water volumes 250-500 l/ha) and 0.025 or 0.038 kg ai/hl (high-volume spraying, water volume 1500 l/ha). The rate per area was either 0.38 or 0.56 kg ai/ha. Four trials were with 3 treatments and 10 trials with 5. The spray intervals were generally 7-14 days. In 8 trials all treatments were after flowering; in the others one treatment was applied before and/or during flowering and the others after flowering. In all trials with 5 applications, cherries were sampled at the GAP PHI of 21 days.

Two trials were conducted in northern and 4 in southern France, all on sweet cherries, with 2 treatments at a spray concentration of 0.03 kg ai/hl corresponding to 0.3 kg ai/ha (water volume 925-1000 l/ha) and a PHI of 7 days. Samples were also collected on days 3, 10, and 14. The interval between the 2 treatments was 13-15 days. The applications were carried out during the development and maturity of the fruit.

Table 27. Residues of bitertanol from supervised trials on cherries.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl					
10300-82 Germany, 1982	Schatten-morelle (sour)	25 WP	0.38	250 (1500)[2]	0.15 (0.025)[2]	3 (3)[1]	81	fruit without stone	0 14 28 35 42	1.2 0.27 0.1 0.06 0.05
10301-82 Germany, 1982	Schatten-morelle	25 WP	0.38	250 (1500)	0.15 (0.025)[2]	3 (3)[1]	79	fruit without stone	0 14 28 35 42	3.2 0.34 0.07 0.07 <0.05
10302-82 Germany, 1982	Schatten-morelle	25 WP	0.38	250 (1500)[2]	0.15 (0.025)[2]	3 (3)[1]	77	fruit without stone	0 14 28 35 42	11 2.3 0.68 0.36 0.58
10303-82 Germany, 1982	Schatten-morelle	25 WP	0.38	250	0.15	3 (3)[1]	77	fruit without stone	0 14 28 35	4.0 0.65 0.21 0.12
10312-86 Germany, 1986	Schatten-morelle	500 SC	0.56	1500	0.038	5 (3)[1]	71	fruit without stone	0 7 14 21 28	14 5.9 3.6 0.48 0.85
10313-86 Germany, 1986	Schatten-morelle	500 SC	0.56	1500	0.038	5 (4)[1]	77	fruit without stone	0 7 14 21 28	6.2 0.8 0.96 0.35 0.68

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl					
10315-86 Germany, 1986	Schatten-morelle	500 SC	0.56	300 (1500)[2]	0.19 (0.038)[2]	5 (4)[1]	77	fruit without stone	0	8.9
									7	1.8
									14	2.0
									21	0.83
									28	0.63
10311-87 Germany, 1987	Schatten-morelle	500 SC	0.56	1500	0.038	5 (5)[1]	77	fruit without stone	0	1.0
									7	0.61
									14	0.24
									21	0.2
									28	0.19
10313-87 Germany, 1987	Schatten-morelle	500 SC	0.56	300 (1500)[2]	0.19 (0.038)[2]	5 (5)[1]	77	fruit without stone	0	2.8
									7	1.2
									14	0.84
									21	0.44
									28	0.37
10314-87 Germany, 1987	Schatten-morelle	500 SC	0.56	300 (1500)[2]	0.19 (0.038)[2]	5 (3)[1]	81	fruit without stone	0	7.1
									7	3.4
									14	0.8
									21	0.52
									28	0.49
0206-89 Germany, 1989	Heimanns Rubin (sour)	500 SC	0.38	1500	0.025	5 (5)[1]	81	fruit without stone	0	0.93
									7	0.38
									14	0.25
									21	0.31
									28	0.30
0207-89 Germany, 1989	Schatten-morelle	500 SC	0.38	1500	0.025	5 (4)[1]	85	fruit without stone	0	1.5
									7	0.98
									14	0.85
									20	0.19
								whole fruit, calculated	7	0.81
									14	0.77
									20	0.17
0209-89 Germany, 1989	Schatten-morelle	500 SC	0.38	500 (1500)[2]	0.08 (0.027)[2]	5 (5)[1]	81	fruit without stone	0	1.1
									7	0.84
									14	0.46
									21	0.39
									28	0.44
0210-89 Germany, 1989	Schatten-morelle	500 SC	0.38	500 (1500)[2]	0.08 (0.027)[2]	5 (4)[1]	83	fruit without stone	0	1.9
									7	0.52
									14	0.36
									21	0.36
									28	0.24
								whole fruit, calculated	7	0.43
									14	0.31
									21	0.32
									28	0.22

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl					
RA-2113/96 0746-96 N. France, 1996	Sunburst (sweet)	500 SC	0.3	1000	0.03	2	83	fruit with stone	0 3 7 10 14	0.33 0.20 0.22 0.14 0.15
RA-2113/96 0747-96 N. France, 1996	Marmotte (sweet)	500 SC	0.28 0.3	925 1000	0.03 0.03	1 1	87	fruit with stone	0 3 7 10 14	0.31 0.26 0.14 0.29 0.13
RA-2113/96 0680-96 S. France, 1996	Napoleon (sweet)	500 SC	0.3	1000	0.03	2	81	fruit with stone	0 3 7 10 14	0.95 0.57 0.46 0.36 0.37
RA-2113/96 0681-96 S. France, 1996	Van (sweet)	500 SC	0.3	1000	0.03	2	77	fruit with stone	0 3 7 10 14	0.53 0.21 0.13 0.06 0.08
RA-2113/96 0682-96 S. France, 1996	Belge (sweet)	500 SC	0.3	1000	0.03	2	77	fruit with stone	3 7 10 14	0.40 0.38 0.17 0.15
RA-2113/96 0683-96 S. France, 1996	Starking-son (sweet)	500 SC	0.3	1000	0.03	2	83	fruit with stone	0 3 7 14	0.43 0.24 0.15 0.14

[1](no. of treatments): applications after flowering
[2]kg ai/hl calculated for 1500 l water/ha

Plums (Table 28). The use of bitertanol in plums is registered in Belgium, France, Italy, Poland, Portugal and Switzerland.

Twelve trials in Germany were with 5 applications, at about 7- or 14-day intervals, with both high- and low-volume (atomizing) spraying. Water volumes were 1000 l/ha at a concentration of 0.038 kg/hl or 1500 l/ha at a concentration of 0.025 or 0.038 kg ai/hl, giving rates of 0.38 or 0.56 kg ai/ha. Water volumes of 300 l/ha at 0.125 kg ai/hl or 500 l/ha at 0.075 kg ai/hl both gave 0.38 kg ai/ha. In 6 trials all applications were after flowering with spray intervals of about 7 or 14 days. In the other six trials 2 applications were during and shortly after flowering.

In southern Europe four residue trials were in France and one in Portugal, with 3 applications at a concentration of 0.03 kg ai/hl. With a water volume of 1000 l/ha this corresponded to 0.3 kg ai/ha. The treatments were during fruit development and fruit maturity at intervals of 13-14 days.

Table 28. Residues of bitertanol from supervised trials on plums.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10328-81 Germany, 1981	Bühler-früh-zwetsche	300 EC	0.56	1500	0.038	5 (5)[1]	fruit colouring	fruit without stone	0	2.7
									7	1.3
									10	2.2
									14	1.4
									21	1.8
								whole fruit, calculated	0	2.6
									7	1.2
									10	2.1
									14	1.3
									21	1.7
10329-81 Germany, 1981	Haus-zwetsche	300 EC	0.56	1500	0.038	5 (5)[1]	85	fruit without stone	0	2.2
									7	1.5
									10	1.5
									14	0.89
									21	0.72
								whole fruit, calculated	0	2.1
									7	1.4
									10	1.4
									14	0.85
									21	0.69
10330-81 Germany, 1981	Ortenauer	300 EC	0.38	1000	0.038	5 (5)[1]	85	fruit without stone	0	1.1
									7	1.0
									10	0.59
									14	0.59
									21	0.24
10356-81 Germany, 1981	Haus-zwetsche	300 EC	0.38	1000	0.038	5 (5)[1]	85	fruit without stone	0	1.8
									7	1.5
									10	1.6
									14	0.83
									21	1.4
								whole fruit, calculated	10	1.5
									14	0.79
									21	1.3
0230-88 Germany, 1988	Haus-zwetsche	500 SC	0.38	1500	0.025	5 (4)[1]	88	fruit without stone	0	0.39
									7	0.32
									14	0.33
									21	0.22
0232-88 Germany, 1988	Haus-zwetsche	500 SC	0.38	1500	0.025	5 (3)[1]	88	fruit without stone	0	0.21
									7	0.17
									14	0.21
									21	0.21
									28	0.11

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
0233-88 Germany, 1988	Auer-bacher	500 SC	0.38	300 (1500)[2]	0.125 (0.025)[2]	5 (3)[1]	75	fruit without stone	0 7 14 21 28	0.07 0.07 <u>0.04</u> <0.02 <0.02
0234-88 Germany, 1988	Haus-zwetsche	500 SC	0.38	300 (1500)[2]	0.125 (0.025)[2]	5 (3)[1]	76	fruit without stone	0 7 14 21 28	1.7 1.1 0.92 0.92 <u>0.94</u>
0220-89 Germany, 1989	Auer-bacher	500 SC	0.38	1500	0.025	5 (3)[1]	77	fruit without stone	0 7 14 21 28	0.31 0.19 0.13 <u>0.16</u> 0.07
0221-89 Germany, 1989	Haus-zwetsche	500 SC	0.38	1500	0.025	5 (5)[1]	88	fruit without stone whole fruit, calculated	0 7 14 21 28 0 7 14 21 28	0.72 0.45 <u>0.58</u> 0.33 0.40 0.69 0.43 0.55 0.31 0.40
0222-89 Germany, 1989	Ortenauer	500 SC	0.38	500 (1500)[2]	0.075 (0.025)[2]	5 (3)[1]	77	fruit without stone	0 7 14 21 28	0.19 0.27 0.11 <u>0.15</u> 0.12
0384-89 Germany, 1989	Auer-bacher	500 SC	0.38	500 (1500)[2]	0.075 (0.025)[2]	5 (3)[1]	76	fruit without stone	0 7 14 21 28	0.18 0.13 <u>0.19</u> 0.11 0.08
10301-80 S. France, 1980	Prunier d‘ Ente	25 WP	0.25	1000 (1500)[2]	0.03 (0.02)[2]	3	87	fruit without stone whole fruit, calculated	9 14 9 14	<u>0.49</u> 0.39 0.45 0.34
RA-2112/96 606855 S. France, 1996	Reine Claude	500 SC	0.3	1000 (1500)[2]	0.03 (0.02)[2]	3	77	fruit with stone	0 3 7 10 14	0.16 0.11 0.07 <u>0.09</u> 0.05
RA-2112/96 606863 S. France, 1996	Prune de‘ ente	500 SC	0.3	1000 (1500)[2]	0.03 (0.02)[2]	3	83	fruit with stone	0 3 7 14	0.41 0.38 0.26 <u>0.34</u>

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
RA-2112/96 606871 S. France, 1996	Quetsche	500 SC	0.3	1000 (1500)[2]	0.03 (0.02)[2]	3	81	fruit with stone	0 3 7 14	0.45 0.33 <u>0.36</u> 0.28
RA-2112/96 606847 Portugal, 1996	Red Beauty	500 SC	0.3	1000 (1500)[2]	0.03 (0.02)[2]	3	81	fruit with stone	0 3 7 10 14	<0.02 <0.02 <0.02 <0.02 <0.02

[1]no. of treatments after flowering
[2]kg ai/hl calculated for 1500 l water/ha

<u>Peaches and nectarines</u> (Tables 29 and 30). The use of bitertanol is registered in southern Europe and South Africa.

Three trials on nectarines were conducted in Italy and two in southern France. The spray concentration was 0.019 kg ai/hl in 4 trials and 0.018 kg ai/hl in the fifth, corresponding to 0.25 or 0.26 kg ai/ha (water volume 1300-1400 l/ha). The nectarine trees were sprayed once in three trials and twice in the other two at an interval of 7 or 10 days. The final treatment was 7 days before harvest in all the trials.

In South Africa 2 trials were carried out with 4 applications at 0.012 or 0.025 kg ai/hl. The concentration of 0.012 kg ai/hl corresponded to 0.3 kg ai/ha (water volume 2500 l/ha). The spraying intervals were 18-24 days. In a third trial there were 2 applications at a concentration of 0.012 kg ai/hl, equivalent to 0.36 kg ai/ha (water 3000 l/ha). The spraying interval was 14 days.

In 6 residue trials on peaches in Spain and 1 in Portugal there were 3 applications: at flowering, at development of the fruit, and at maturity. The spray concentration was 0.038 or 0.030 kg ai/hl. This corresponded to 0.25-0.38 kg ai/ha for the first application (water volume 660-1000 l/ha), 0.24-0.51 kg ai/ha for the second application (water volume 800-1500 l/ha), and 0.3-0.71 kg ai/ha for the third (water volume 1000-1900 l/ha).

In South Africa 2 trials were with 3 treatments at either 0.0125 or 0.025 kg ai/hl sprayed to run-off. Assuming a water rate of 2000 l/ha this would correspond to 0.25 or 0.5 kg ai/ha. Four other trials were with 1 or 2 treatments at either 0.012 or 0.024 kg ai/hl, corresponding to 0.24 or 0.48 kg ai/ha (water volume 2000 l/ha).

Table 29. Residues of bitertanol from supervised trials on nectarines.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10360-85 Italy, 1985	Stark Red Gold	25 WP	0.26	1400	0.019	2	85	fruit without stone	7 11 18	<u>0.13</u> 0.1 0.13
10361-85 Italy, 1985	Fantasia	25 WP	0.26	1400	0.019	1	85	fruit without stone	7 12 18	<u>0.23</u> 0.21 0.23

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10362-85 Italy, 1985	Stark Red Gold	25 WP	0.26	1400	0.019	1	85	fruit without stone	7 11 18	0.25 0.21 0.21
10363-85 S. France, 1985	Fantasia	25 WP	0.25	1400	0.018	2	fruit diameter 60 mm	fruit without stone	0 7 14	0.31 0.20 0.13
10365-85 S. France, 1985	Fantasia	25 WP	0.25	1320	0.019	1	85	fruit without stone	0 7 14	0.1 0.12 <0.05
311/88419/ W212-A South Africa, 1982		300 EC	0.3	2500	0.012	4	-	fruit without stone	0 3 10 14 24	0.53 0.47 0.21 0.18 0.18
311/88419/ W212-B South Africa, 1982		300 EC	0.6	2500	0.025	4	-	fruit without stone	0 3 10 14 24	1.5 0.68 0.54 0.51 0.37
311/88933/ C181 South Africa, 1985		300 EC	0.36	2990	0.012	2	-	fruit without stone	0 7 14 21 28 35 42 49 56	1.9 1.4 0.60 0.31 0.20 0.10 0.16 0.17 0.08

Table 30. Residues of bitertanol from supervised trials on peaches.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
RA-2011/93 303305 Spain, 1993	Caterine	25 WP	0.37 0.45	992 1203	0.038 0.038	1 2	85	fruit without stone whole fruit, calculated	0 3 7 10 14 10 14	0.41 0.67 0.46 0.42 0.43 0.40 0.41
RA-2011/93 303380 Spain, 1993	Maycrest	25 WP	0.34 0.38	900 1000	0.038 0.038	1 2	85	fruit without stone whole fruit, calculated	0 14 14	1.2 0.74 0.71

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
RA-2083/94 403423 Spain, 1994	July Lady	25 WP	0.38 0.45 0.61	1000 1187 1625	0.038 0.038 0.038	1 1 1	82	fruit without stone whole fruit, calculated	0 3 7 10 14 0 3 7 10 14	0.39 0.30 0.29 <u>0.27</u> 0.19 0.36 0.28 0.27 0.26 0.18
RA-2083/94 403431 Spain, 1994	Merril Gem Free	25 WP	0.25 0.38 0.47	666 1000 1250	0.038 0.038 0.038	1 1 1	84	fruit without stone whole fruit, calculated	0 3 7 10 14 7 10 14	0.62 0.47 0.43 <u>0.54</u> 0.23 0.39 0.49 0.21
RA-2083/94 405167 Spain, 1994	Baby Gold 9	25 WP	0.29 0.51 0.72	762 1371 1905	0.038 0.038 0.038	1 1 1	81	fruit without stone whole fruit, calculated	0 14 14	0.71 <u>0.26</u> 0.24
RA-2111/96 606901 Spain, 1996	Mira-flores	500 SC	0.30 0.45 0.45	997 1491 1510	0.03 0.03 0.03	1 1 1	81-85	fruit with stone	0 3 7 10 14	0.10 0.10 0.10 <u>0.05</u> 0.04
RA-2111/96 606898 Portugal, 1996	Coronado	500 SC	0.25 0.24 0.30	814 800 1000	0.03 0.03 0.03	1 1 1	87	fruit with stone	0 3 7 11 14	0.25 0.32 0.19 0.09 <u>0.10</u>
311/88421/ W214-A South Africa, 1982	Wolte-made	300 EC	-	drip-off	0.0125	3	-	fruit with stone	0 5 11 19 26	0.55 0.35 0.25 0.15 <0.1
311/88421/ W214-B South Africa, 1982	Wolte-made	300 EC	-	drip-off	0.025	3	-	fruit with stone	0 5 19	1.8 1.2 0.5

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
311/88736/ B140-A South Africa, 1985	Kakamas	300 EC	0.24	2000	0.012	1	-	fruit without stone	0	0.62
									7	0.44
									14	0.24
									21	0.14
									28	0.11
									35	0.12
									42	0.07
									49	0.06
									56	0.05
311/88736/ B140-B South Africa, 1985	Kakamas	300 EC	0.24	2000	0.012	2	-	fruit without stone	0	1.3
									7	0.84
									14	0.31
									21	0.27
									28	0.29
									35	0.12
									42	0.06
									49	0.06
									56	0.07
311/88736/ B140-C South Africa, 1985	Kakamas	300 EC	0.48	2000	0.024	1	-	fruit without stone	0	2.0
									7	1.4
									14	0.69
									21	0.60
									28	0.51
									35	0.26
									42	0.23
									49	0.16
									56	0.14
311/88736/ B140-D South Africa, 1985	Kakamas	300 EC	0.48	2000	0.024	2	-	fruit without stone	0	1.8
									7	1.2
									14	1.0
									21	0.66
									28	0.37
									35	0.23
									42	0.31
									49	0.17
									56	0.17

Bananas (Table 31). There are recent registrations for the use of bitertanol on bananas throughout Central America, and in the Philippines, Taiwan, and Cameroon.

In Central America, residue trials were conducted in Costa Rica and Honduras with 9-16 applications, usually 12, at intervals of 8-15 days, usually 10. Application rates were 0.12-0.13 kg ai/ha (4 trials), 0.24-0.25 kg ai/ha (6 trials), and 0.29-0.3 kg ai/ha (6 trials). The treatments were high-volume (473 l/ha), low-volume (60-120 l/ha) or ultra-low-volume (19 l/ha). In order to cover all common use conditions, both bagged and unbagged fruit were included (as the bags may be torn during the growing season, possibly resulting in higher residues than would otherwise be expected). Both green and ripened fruit were analysed in 6 trials, and both washed and unwashed samples in 10 trials.

Six trials were carried out in the Philippines and Taiwan, four with bagged and two with unbagged fruit. The use patterns were 26 × 0.2 kg ai/ha, 10 × 0.3 kg ai/ha and 12 × 0.04 kg ai/ha. In the Philippines the applications were by air, as recommended on the label (water volume 23-29 l/ha). In Taiwan the water volume was 40 l/ha.

In 2 trials in Cameroon bagged bananas were sprayed by air either 5 or 8 times with a 250 OF formulation (oil-miscible flowable concentrate or suspension) at 0.25 kg ai/ha, 15 l/ha. Samples were collected either 6 or 12 days after the last application.

Table 31. Residues of bitertanol from supervised trials on bananas.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
10309-78 Costa Rica, 1978	Grand Naine	200 EC	0.25	100	0.25	16	-	pulp, peel, fruit[1]	4	<0.05
10350-80-A Costa Rica, 1980		300EC	0.12	60	0.2	10	before harvest, bagged	pulp, peel, fruit	8	<0.01
10350-80-B Costa Rica, 1980		300EC	0.12	60	0.2	10	before harvest, unbagged	pulp peel fruit	8	0.014 0.15 0.055
10330-80-A Costa Rica, 1980	Grand Naine	300EC	0.24	120	0.2	10	before harvest, bagged	pulp peel fruit	8	<0.01 0.039 0.015
10330-80-B Costa Rica, 1980	Grand Naine	300EC	0.24	120	0.2	10	before harvest, unbagged	pulp peel fruit	8	0.019 0.12 0.047
68896 Honduras, 1980	Cavendish	300EC	0.13	19	0.69	12	bagged	pulp w-[2] pulp w+[3] peel w- peel w+ fruit w- fruit w+	0	0.01 0.02 0.02 0.03 0.01 0.02
68897 Honduras, 1980	Cavendish	300EC	0.13	19	0.69	12	unbagged	pulp w- pulp w+ peel w- peel w+ fruit w- fruit w+	0	0.04 0.04 0.19 0.20 0.10 0.10
68898 Honduras, 1980	Cavendish	300EC	0.25	19	1.3	12	bagged	pulp w- pulp w+ peel w- peel w+ fruit w- fruit w+	0	<0.01 <0.01 0.05 0.03 0.03 0.02

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
68899 Honduras, 1980	Cavendish	300EC	0.25	19	1.3	12	unbagged	pulp w- pulp w+ peel w- peel w+ fruit w- fruit w+	0	0.13 0.11 0.64 0.41 0.32 0.23
68900 Honduras, 1980	Cavendish	25 WP	0.25	19	1.3	12	unbagged bagged	pulp peel fruit pulp fruit	0	0.03 0.10 0.06 0.02 0.03
80469-A Costa Rica, 1981	Grand Nain	300EC	0.29	66	0.44	9	harvest stage, bagged	pulp gr.[4], w- pulp ri.[5], w- pulp gr., w+ pulp ri., w+ peel gr., w- peel ri., w- peel gr., w+ peel ri., w+ fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+	3	<0.01 <0.01 0.01 0.02 <0.01 <0.01 0.05 0.05 <0.01 <0.01 0.03 0.03
80469-B Costa Rica, 1981	Grand Nain	300EC	0.29	66	0.44	9	harvest stage, unbagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+ peel gr., w- peel ri., w- peel gr., w+ peel ri., w+ fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+	3	0.11 0.06 0.09 0.11 0.53 0.25 0.41 0.45 0.24 0.13 0.22 0.23

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
80472 Honduras, 1981	Grand Nain	300EC	0.29	473	0.06	12	harvest stage, bagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+ peel gr., w- peel ri., w- peel gr., w+ peel, ri., w+ fruit gr., w- fruit ri., w- fruit gr., w+ fruit, ri., w+	0	0.01 0.01 0.02 0.02 0.04 0.03 0.04 0.08 0.02 0.02 0.03 0.04
80473 Honduras, 1981	Grand Nain	300EC	0.29	473	0.06	12	harvest stage, unbagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+ peel gr., w- peel ri., w- peel gr., w+ peel ri., w+ fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+	0	0.08 0.08 0.17 0.14 0.76 0.32 0.73 0.51 0.33 0.17 0.36 0.28
80470 Honduras, 1981	Grand Nain	50 WP	0.3	473	0.06	12	harvest stage, bagged	pulp ri., w- pulp gr., w+ pulp ri., w+ peel ri., w- peel gr., w+ peel ri., w+ fruit ri., w- fruit gr., w+ fruit ri., w+	0	0.01 0.01 <0.01 0.12 0.15 0.03 0.05 0.06 0.01

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage, bagged or unbagged	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water l/ha	kg ai/hl					
80471 Honduras, 1981	Grand Nain	50 WP	0.3	473	0.06	12	harvest stage, unbagged	pulp gr., w- pulp ri., w- pulp gr., w+ pulp ri., w+ peel gr., w- peel ri., w- peel gr., w+ peel ri., w+ fruit gr., w- fruit ri., w- fruit gr., w+ fruit ri., w+	0	0.03 <0.01 0.03 0.02 0.10 0.03 0.09 0.05 0.06 0.01 0.05 0.03
10320-80 Philippines, 1980	Giant Cavendish	200 EC	0.2	29	0.69	26	green, bagged	pulp, peel, fruit pulp, peel fruit	0 11	<0.05 <0.05
10321-80 Philippines, 1980	Giant Cavendish	200 EC	0.2	23	0.87	26	green, bagged	pulp, peel, fruit pulp, peel, fruit	0 11	<0.05 <0.05
10344-81 Philippines, 1981	Dwarf Cavendish	300 EC	0.30	24	1.25	10	ripe for cutting, bagged	pulp peel fruit	2	<0.01 0.019 <0.01
10345-81 Philippines, 1981	Dwarf Cavendish	300 EC	0.30	24	1.25	10	ripe for cutting, unbagged	pulp peel fruit	2	0.015 0.14 0.06
10350-81-A Taiwan, 1981	native variety	300 EC	0.038	40	0.094	12	before harvest, bagged	pulp peel fruit	0	<0.01 0.09 <0.01
10350-81-B Taiwan, 1981	native variety	300 EC	0.038	40	0.094	12	before harvest unbagged	pulp peel fruit	0	0.14 2.1 0.51
10366-81-A Cameroon, 1981	Poyo	250 OF	0.25	15 + oil	1.7	5	bagged	pulp peel fruit	6	<0.01 0.01 <0.01
10366-81-B Cameroon, 1981	Poyo	250 OF	0.25	15 + oil	1.7	8	bagged	pulp, peel, fruit	12	<0.01 <0.01 <0.01

[1]fruit: whole fruit, residue calculated from peel and pulp
[2]w- : unwashed
[3]w+ : washed
[4]gr.: green
[5]ri. : ripened

Tomatoes (Table 32).The use of bitertanol on tomatoes grown in greenhouses is authorised in Belgium and The Netherlands.

There were 8 trials in the Netherlands and 2 in Belgium with three treatments at intervals of 4-6 days. Two of the trials were with cherry tomatoes.

Table 32. Residues of bitertanol from supervised trials on greenhouse tomatoes.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
0304-88 The Netherlands, 1988	Calipso	300 EC	0.9	3000	0.03	3	87-89	0 1 3 5 7	0.90 0.96 0.96 0.90 0.77
0305-88 The Netherlands, 1988	Nr. 704	300 EC	0.75	2500	0.03	3	87-89	0 1 3 5 7	1.1 1.0 0.98 0.90 0.87
0306-88 The Netherlands, 1988	Calipso	300 EC	0.6	2000	0.03	3	87-89	0 1 3 5 7	0.95 1.2 0.91 0.96 0.90
RA-2010/91 101796 The Netherlands, 1991	Evita (cherry)	300 EC	0.9	3000	0.03	3	A[1]	0 1 3 5 7	1.8 2.3 1.6 2.1 1.7
RA-2010/91 101818 The Netherlands, 1991	Viscon	300 EC	0.9	3000	0.03	3	A	0 1 3 5 7	0.61 0.66 0.52 0.56 0.51
RA-2010/91 104817 The Netherlands, 1991	Evita (cherry)	300 EC	0.9	3000	0.03	3	A	0 1 3 5 7	2.3 2.8 2.4 2.1 2.2
RA-2059/96 605557 Belgium, 1996	Macua	500 SC	0.6	2000	0.03	3	A	0 3	0.62 0.54
RA-2059/96 605565 Belgium, 1996	Macua	500 SC	0.6	2000	0.03	3	A	0 3	0.52 0.48
RA-2059/96 605573 The Netherlands, 1996	Aromate	500 SC	0.6	2200	0.027	3	A	0 3	0.61 0.39

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RA-2059/96 605581 The Netherlands, 1996	Jamaica	500 SC	0.6	2000	0.03	3	A	0 3	0.45 0.41

[1]A: Several stages of fruit development on the same plant at the same time

Cucumbers (Table 33). At present the use of bitertanol on cucumbers grown in greenhouses is registered in Belgium, The Netherlands and Italy.

Eight greenhouse trials in The Netherlands were with 3 applications at intervals of 5-6 days and 2 in southern France were with 3 applications at intervals of 14 days.

The French trials approximated Italian GAP. The trials in The Netherlands complied with their critical national GAP.

Table 33. Residues of bitertanol from supervised greenhouse trials on cucumbers.

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
10304-80 S. France, 1980	Pendorax	25 WP	0.35	1875	0.02	3	87-89	17	<0.05
10304-80 S. France, 1980	Pendorax	25 WP	0.41	2200	0.02	3	85-87	17	<0.05
0561-88 The Netherlands, 1988	Sandra	300 EC	0.9	3000	0.03	3	87-89	0 1 2 3 5	0.25 0.22 0.21 0.22 0.18
0562-88 The Netherlands, 1988	Mustang	300 EC	0.9	3000	0.03	3	87-89	0 1 2 3 5	0.47 0.38 0.29 0.21 0.16
RA-2096/96 605603 The Netherlands, 1996	Escape	500 SC	0.6	2000	0.03	3	A[1]	0 3	0.36 0.22
RA-2096/96 606611 The Netherlands, 19956	Flamige	500 SC	0.6	2000	0.03	3	A	0 3	0.21 0.10

Report no. Country Year	Variety	Form.	Application rate per treatment			No. of treat-ments	Growth stage	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RA-2096/96 605638 The Netherlands, 1996	Venturea	500 SC	0.6	2000	0.03	3	A	0 3	0.19 0.16
RA-2096/96 605646 The Netherlands, 1996	Jessica	500 SC	0.53 0.55 0.62	1771 1823 2057	0.03 0.03 0.03	3	A	0 3	0.28 0.17
RA-2096/96 606654 The Netherlands, 1996	Ducan	500 SC	0.6	2000	0.03	3	A	0 1 3 5 7	0.34 0.24 0.19 0.12 0.06
RA-2096/96 606662 The Netherlands, 1996	Suprami	500 SC	0.86 0.77 0.86	2868 2689 2868	0.03 0.03 0.03	3	A	0 1 3 5 7	0.18 0.16 0.11 0.06 0.05

[1]A: Several stages of fruit development on the same plant at the same time

Seed treatments

Barley (Table 34).The use of bitertanol as a seed dressing on barley is authorised in France, The Netherlands and Sweden.

Eight residue trials were conducted on spring barley in Germany, 3 with the 39.8 DS formulation, 3 with 298 LS, and 2 with 375 FS. Application rates were 57-75 g ai/100 kg seed. Forage was sampled 67-94 days after seed treatment and drilling, and straw and grain at harvest, 100-144 days after treatment.

Table 34. Residues of bitertanol from supervised trials on spring barley after seed treatment.

Report, Country Year	Variety	Form.	Application rate kg ai/100 kg seed	No. of treatments	Sample	PHI, days	Residues, mg/kg
10200-83 Germany 1983	Carina	39.8 DS[1]	0.075	1	forage grain straw	74 100 100	<0.05 <0.05 <0.05
10201-83 Germany 1983	Carina	39.8 DS[1]	0.075	1	forage grain straw	67 103 103	<0.05 <0.05 <0.05
10202-83 Germany 1983	Carina	39.8 DS[1]	0.075	1	forage grain straw	94 140 140	<0.05 <0.05 <0.05
10245-83 Germany 1983	Koral	375 FS[2]	0.057	1	forage grain straw	86 128 128	<0.05 <0.05 <0.05

Report, Country Year	Variety	Form.	Application rate kg ai/100 kg seed	No. of treatments	Sample	PHI, days	Residues, mg/kg
10246-83 Germany 1983	Koral	375 FS[2]	0.057	1	forage grain straw	86 128 128	<0.05 <0.05 <0.05
10202-84 Germany 1984	Carina	298 LS[3]	0.07	1	forage grain straw	89 135 135	<0.05 <0.05 <0.05
10203-84 Germany 1984	Aura	298 LS[3]	0.07	1	forage grain straw	84 144 144	<0.05 <0.05 <0.05
10204-84 Germany 1984	Carina	298 LS[3]	0.07	1	forage grain straw	80 131 131	<0.05 <0.05 <0.05

[1] 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole
[2] 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole
[3] 298 LS : 280 g/l bitertanol + 18 g/l fuberidazole

Oats (Table 35). Bitertanol seed dressings are registered in Austria, France, Germany, the UK, The Netherlands, Poland and Sweden.

In 7 residue trials in Germany, oat seeds were treated with a 39.8 DS, 375 FS, or 398 FS formulation at 56-75 g ai/t. Forage, straw and grain were collected in all trials, and also ears in 3 trials. Forage was sampled 63-101 days, ears 75-95 days and straw and grain 113-147 days after seed treatment and drilling.

Table 35. Residues of bitertanol from supervised trials on oats after single seed treatments.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10366-82 Germany, 1982	Flämings-krone	39.8 DS[1]	0.075	forage ears grain straw	76 86 86 139 139	<0.1 <0.1 <0.05 <0.05 <0.05
10367-82 Germany, 1982	Flämings-krone	39.8 DS[1]	0.075	forage ears grain straw	63 75 75 131 131	<0.1 <0.1 <0.05 <0.05 <0.05
10368-82 Germany, 1982	Flämings-krone	39.8 DS[1]	0.075	forage ears grain straw	67 95 95 147 147	<0.1 <0.1 <0.05 <0.05 <0.05
10241-83 Germany, 1983	Flämings Nova	375 FS[2]	0.057	forage grain straw	101 136 136	<0.05 <0.05 <0.05
10242-83 Germany, 1983	Flämings Nova	375 FS[2]	0.057	forage grain straw	75 113 113	<0.05 <0.05 <0.05

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10212-83 Germany, 1983	Flämings Nova	398 FS[3]	0.055	forage grain straw	94 140 140	<0.05 <0.05 <0.05
10213-83 Germany, 1983	Flämings Nova	398 FS[3]	0.056	forage grain straw	97 141 141	<0.05 <0.05 <0.05

[1] 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole
[2] 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole
[3] 398 FS : 375 g/l bitertanol + 23 g/l fuberidazole

Rye (Table 36). Seed dressings containing bitertanol are registered for use on rye in Austria, Denmark, France, Germany, the UK, The Netherlands, Poland and Sweden.

In 9 residue trials on winter rye in Germany the formulations were 39.8 DS, 375 FS, 398 FS, and 298 LS. The application rate was 56 or 57 g ai/t in 8 trials and 70 g ai/t in the 9th. Samples of forage were collected 218-269 days, and grain and straw 289-322 days after seed treatment and drilling. Samples of ears were also collected in 4 trials after 228-269 days.

Table 36. Residues of bitertanol from supervised trials on rye after single seed treatments.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10363-82 Germany, 1981/82	Carokurz	39.8 DS[1]	0.056	forage ears grain straw	219 228 228 297 297	<0.1 <0.1 <0.05 <0.05 <0.05
10364-82 Germany, 1981/82	Carokurz	39.8 DS[1]	0.056	forage ears grain straw	220 231 231 291 291	<0.1 <0.1 <0.05 <0.05 <0.05
10365-82 Germany, 1981/82	Carokurz	39.8 DS[1]	0.056	forage ears grain straw	244 269 269 322 322	<0.1 <0.1 <0.05 <0.05 <0.05
10372-82 Germany, 1981/82	Kustro	398 FS[2]	0.056	forage ears grain straw	254 254 308 308	<0.1 <0.05 <0.05 <0.05
10210-83 Germany, 1982/83	Carokurz	398 FS[2]	0.056	forage grain straw	224 295 295	<0.05 <0.05 <0.05
10211-83 Germany, 1982/83	Carokurz	398 FS[2]	0.056	forage grain straw	220 291 291	<0.05 <0.05 <0.05
10240-83 Germany, 1982/83	Carokurz	375 FS[3]	0.057	forage grain straw	224 295 295	<0.05 <0.05 <0.05

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10200-85 Germany, 1984/85	Carokurz	298 LS[4]	0.056	forage grain straw	220 295 295	<0.05 <0.05 <0.05
10202-85 Germany, 1984/85	Carokurz	298 LS[4]	0.070	forage grain straw	218 289 289	<0.05 <0.05 <0.05

[1] 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole
[2] 398 FS : 375 g/l bitertanol + 23 g/l fuberidazole
[3] 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole
[4] 298 LS : 280 g/l bitertanol + 18 g/l fuberidazole

Wheat (Tables 37, 38). The use of bitertanol seed dressings is currently authorized in Austria, Belgium, Denmark, France, Germany, the UK, The Netherlands and Sweden.

There were 13 trials in Germany, 11 on spring wheat and 2 on winter wheat. The formulations were 39.8 DS, 199 FS, 375 FS, 398 FS, and 298 LS.

Table 37. Residues of bitertanol from supervised trials on spring wheat after seed treatment.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10341-80 Germany, 1980	Kolibri	39.8 DS[1]	0.075	forage ears grain straw straw	76 90 153 90 153	<0.1 <0.1 <0.1 <0.1 <0.1
10342-80 Germany, 1980	Kolibri	39.8 DS[1]	0.075	forage ears grain straw straw	76 90 154 90 154	<0.1 <0.1 <0.1 <0.1 <0.1
10343-80 Germany, 1980	Kolibri	39.8 DS[1]	0.075	forage ears grain straw straw	93 121 177 121 177	<0.1 <0.1 <0.1 <0.1 <0.1
10370-82 Germany, 1982	Kolibri	398 FS[2]	0.075	forage forage ears grain straw	62 77 77 130 130	<0.05 <0.05 <0.05 <0.05 <0.05
10371-82 Germany, 1982	Kolibri	398 FS[2]	0.076	forage forage ears grain straw	56 73 73 134 134	<0.05 <0.05 <0.05 <0.05 <0.05
10243-83 Germany, 1983	Max	375 FS[3]	0.076	forage grain straw	97 143 143	<0.05 <0.05 <0.05

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10244-83 Germany, 1983	Max	375 FS[3]	0.076	forage grain straw	103 147 147	<0.05 <0.05 <0.05
10210-84 Germany, 1984	Kolibri	398 FS[2]	0.075	forage grain straw	104 164 164	<0.05 <0.05 <0.05
10211-84 Germany, 1984	Arkas	398 FS[2]	0.075	forage grain straw	80 142 142	<0.05 <0.05 <0.05
RA-2166/97 707643 Germany, 1997	Thasos	199 FS[4]	0.075	forage grain straw	50 138 138	<0.05 <0.05 <0.05
RA-2166/97 707651 Germany, 1997	Thasos	199 FS[4]	0.075	forage grain straw	42 132 132	<0.05 <0.05 <0.05

[1] 39.8 DS : 37.5 % bitertanol + 2.3 % fuberidazole
[2] 398 FS : 375 g/l bitertanol + 23 g/l fuberidazole
[3] 375 FS : 190 g/l bitertanol + 170 g/l anthraquinone + 15 g/l fuberidazole
[4] 199 FS : 187.5 g/l bitertanol + 11 g/l fuberidazole

Table 38. Residues of bitertanol from supervised trials on winter wheat after single seed treatments.

Report Country Year	Variety	Form.	Application rate, kg ai/100 kg seed	Sample	PHI, days	Residues, mg/kg
10201-85 Germany, 1984/85	Kanzler	298 LS[1]	0.07	forage grain straw	246 323 323	<0.05 <0.05 <0.05
10203-85 Germany, 1984/85	Caribo	298 LS[1]	0.07	forage grain straw	221 285 285	<0.05 <0.05 <0.05

[1] 298 LS : 280 g/l bitertanol + 18 g/l fuberidazole

Livestock feeding studies

Leimkuehler *et al.*, 1984a (Tables 39, 40). Three groups of 3 dairy cows were dosed with bitertanol by bolus capsule for 28 days at levels equivalent to 25, 75 or 250 ppm in the feed on a dry weight basis, or 0.63, 1.88 and 6.25 mg per kg body weight per day based on the initial body weights. Three animals maintained as controls were dosed with vehicle only. At the end of the test period, all the treated animals and one control were slaughtered and their tissues and milk analysed for total extractable residues of bitertanol and its metabolites as 1,2,4-triazole (Leimkuehler *et al.*, 1983).

No dose-related differences between the treated and control animals were evident in food consumption, body weight changes or milk production.

The mean residues in the tissues of the 250 ppm group were liver 2.8 mg/kg, kidneys 0.76 mg/kg, fat 0.84 mg/kg, and muscle 0.32 mg/kg. The residues were correspondingly lower at the lower feeding levels. At 25 ppm the residues averaged 0.63 mg/kg in the liver and were just above the limit of

determination (0.01 mg/kg) in the fat, muscle and kidneys. The residues in the milk reached a plateau after 3-4 weeks in the intermediate-dose group but not in the high-dose group, and were at or below the limit of determination in the 25 ppm group.

Table 39. Residues in tissues of cows dosed with bitertanol for 28 days (Leimkuehler *et al.*,1984a).

Animal no.	Dietary level, ppm	Total residues, mg/kg				Report no.
		Fat	Muscle	Kidneys	Liver	
203	Control	<0.01	<0.01	<0.01	0.01	
205	25	<0.01	<0.01	0.03	0.66	86316,
206	25	0.01	0.02	0.03	0.78	86317,
209	25	0.06	0.06	0.05	0.44	
207	75	0.18	0.08	0.30	1.3	Doc.-No.
210	75	0.16	0.08	0.31	0.87	84-653
212	75	0.16	0.09	0.36	1.9	
201	250	1.3	0.32	0.69	1.9	
208	250	0.89	0.44	1.1	2.7	
211	250	0.36	0.19	0.52	3.7	

Table 40. Residues in milk of cows dosed with bitertanol for 28 days (Leimkuehler *et al.*, 1984a).

Animal no.	Dietary level, ppm	Total residues, mg/kg					Report no.
		Day 0	Day 7	Day 14	Day 21	Day 28	
202	Control						
203	Control	n.a.[1]	n.a.	n.a.	n.a.	<0.01[2]	86316,
204	Control						86317
205	25					<0.01	
206	25	n.a.	n.a.	n.a.	n.a.	<0.01	Doc.-No.
209	25					0.01	84-653
207	75					0.07	
210	75	<0.01[2]	0.09	0.10	0.13	0.03	
212	75					0.02	
201	250					0.25	
208	250	<0.01[2]	0.11	0.19	0.17	0.21	
211	250					0.26	

[1]n.a.: not analysed as residues in later samples were at or below the limit of determination
[2] composite samples

Leimkuehler *et al.*, 1984b (Tables 41, 42). Four groups of 10 laying hens were fed daily rations containing bitertanol at levels of 1, 3, 10 or 100 ppm for 28 days, with ten birds as controls. Ten additional hens were fed the 100 ppm diet for 28 days, then five were maintained on untreated rations for an additional 14 days and three for 28 days before slaughter to determine the rate of decrease of residues.

No sample from the 10 ppm birds were analysed because an interruption in their drinking water supply led to decreased egg production and feed consumption. No significant pesticide-related effects on feed consumption body weight, or egg production occurred.

The tissues and eggs were analysed for total extractable bitertanol and metabolite residues. The samples were extracted with various solvents and acid-hydrolysed to liberate 1,2,4-triazole which was converted to triazolylpinacolone for determination by gas chromatography (Leimkuehler *et al.*, 1983).

Composite samples of tissues and eggs from the 3 ppm and 100 ppm treatment groups were analysed. Eggs were analysed at 7, 14, 21 and 28 days. The residues in tissues from the 100 ppm group were liver 1.03 mg/kg, gizzard 0.23 mg/kg, heart 0.10 mg/kg, muscle 0.07 mg/kg, and fat 0.07 mg/kg.

Liver, gizzard and muscle from the 3 ppm group contained quantifiable residues, highest in the liver at 0.21 mg/kg. The residues in the livers from the 1 ppm feeding level were less than 0.01 mg/kg. Residues in eggs were quantifiable only in the 100 ppm feeding group, reaching 0.11 mg/kg at 28 days. Residues in all samples of eggs, and tissues except liver, were below 0.01 mg/kg 28 days after the birds had been returned to untreated feed. Liver contained 0.04 mg/kg.

Repeat analyses confirmed the original results.

Table 41. Residues in tissues of hens fed on feed containing bitertanol (Leimkuehler *et al.*, 1984b).

Sample	Total residues, mg/kg						Report no.
	28 days[1]				14 days depuration[2]	28 days depuration[2]	
	Control	1 ppm	3 ppm	100 ppm	100 ppm	100 ppm	
Liver	<0.01	<0.01	0.21	1.03	0.05	0.04	86312, 8613, Doc.-No. 84-656
Gizzard	<0.01	n.a.[3]	0.07	0.23	0.02	<0.01	
Muscle	<0.01	n.a.	0.01	0.07	0.07	<0.01	
Fat	<0.01	n.a.	<0.01	0.07	<0.01	<0.01	
Heart	<0.01	n.a.	<0.01	0.10	0.04	<0.01	

[1] composite samples from 10 birds
[2] composite samples from 5 birds at 14 days and 3 at 28 days after removal from fortified feed
[3] n.a.: not analysed because residues were low at higher feeding levels

Table 42. Residues in eggs of hens fed on feed containing bitertanol (Leimkuehler *et al.*, 1984b).

Day	Total residues, mg/kg					Report no.
	Control	1 ppm	3 ppm	100 ppm	100 ppm depuration [3]	
7	n.a.[1]	n.a.[2]	<0.01	0.07	<0.01	86312, 8613, Doc.-No. 84-656
14	n.a.[1]	n.a.[2]	<0.01	0.05	<0.01	
21	n.a.[1]	n.a.[2]	<0.01	0.05	<0.01	
28	<0.01	n.a.[2]	<0.01	0.11	<0.01	

[1] n.a.: not analysed
[2] n.a.: eggs of 1 mg/kg group were not analysed because all residues from 3 mg/kg group were <0.01 mg/kg
[3] analysed 7, 14, 21 and 28 days after removal from fortified feed

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information. Bitertanol is not used on stored products.

In processing

The residues of bitertanol on raw agricultural commodities imply a need for processing studies on fruiting vegetables, pome fruit, and stone fruit. Studies on tomatoes, apples, cherries, peaches and plums were reported.

Tomatoes (Table 43). Washed tomatoes, preserved fruit, juice and dried paste were prepared from tomatoes treated 3 times with bitertanol at 0.9 kg ai/ha (0.03 kg ai/hl) in The Netherlands. The residue after a PHI of 3 days was 0.52 mg/kg.

The processing simulated industrial practice. Washed tomatoes were cut into pieces. The preparation of preserves involved the addition of a pickling liquor (NaCl solution), pasteurization and maceration (Figure 7). To prepare juice and paste, washed tomatoes were blanched in water, the

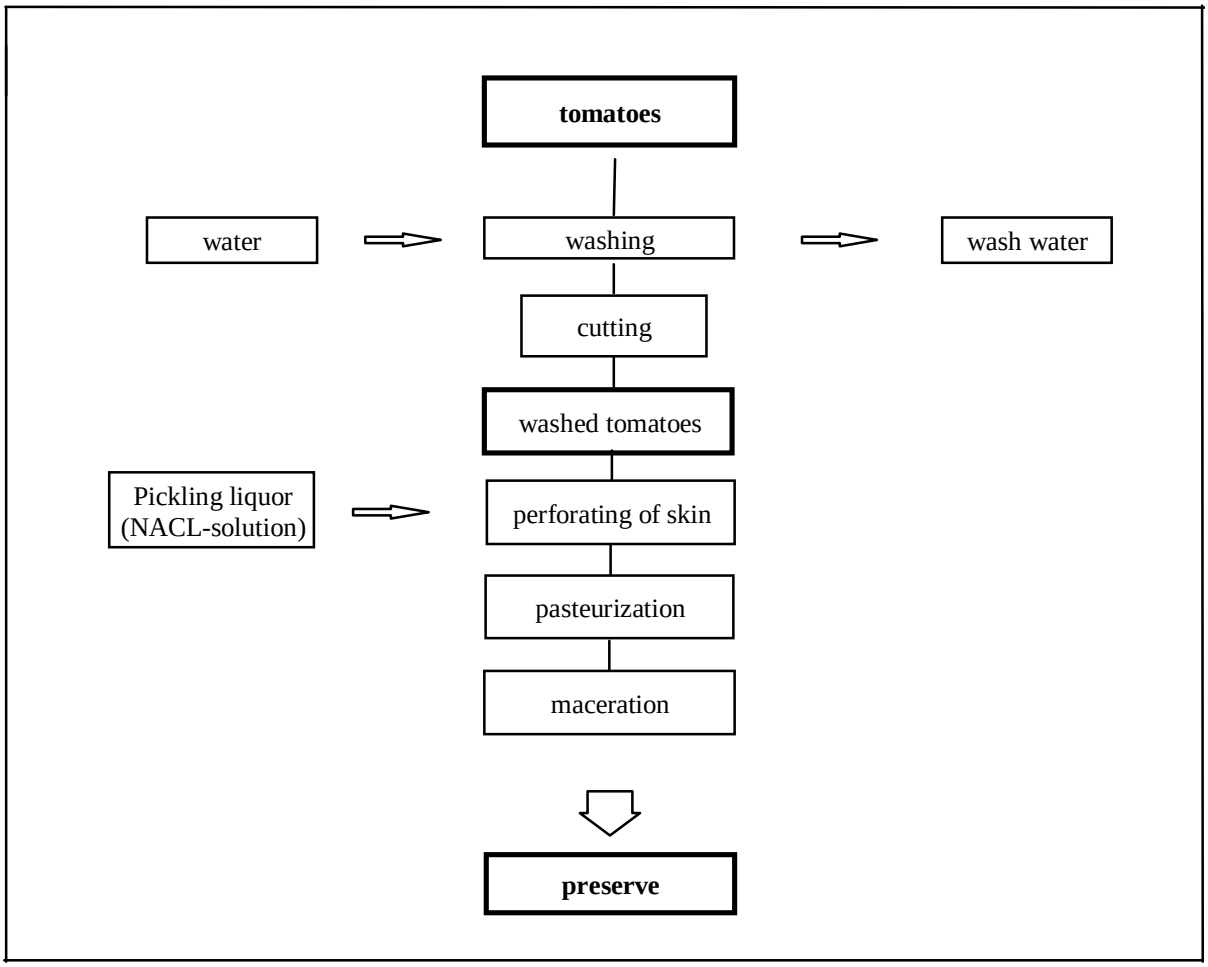
tomato pulp was passed through a strainer and the raw juice separated into two parts for juice and paste. NaCl was added to produce juice which was then pasteurized in an autoclave. To obtain paste the raw juice was concentrated, dried to about 40% dry weight, and finally also pasteurized (Figure 8).

Washing reduced the residues from 0.52 to 0.42 mg/kg. Processing decreased the residues in preserves and juice to 0.19 and 0.07 mg/kg respectively, but concentrated them in paste to 1.1 mg/kg giving a processing factor of 2.1.

Table 43. Bitertanol residues in tomatoes and processed products.

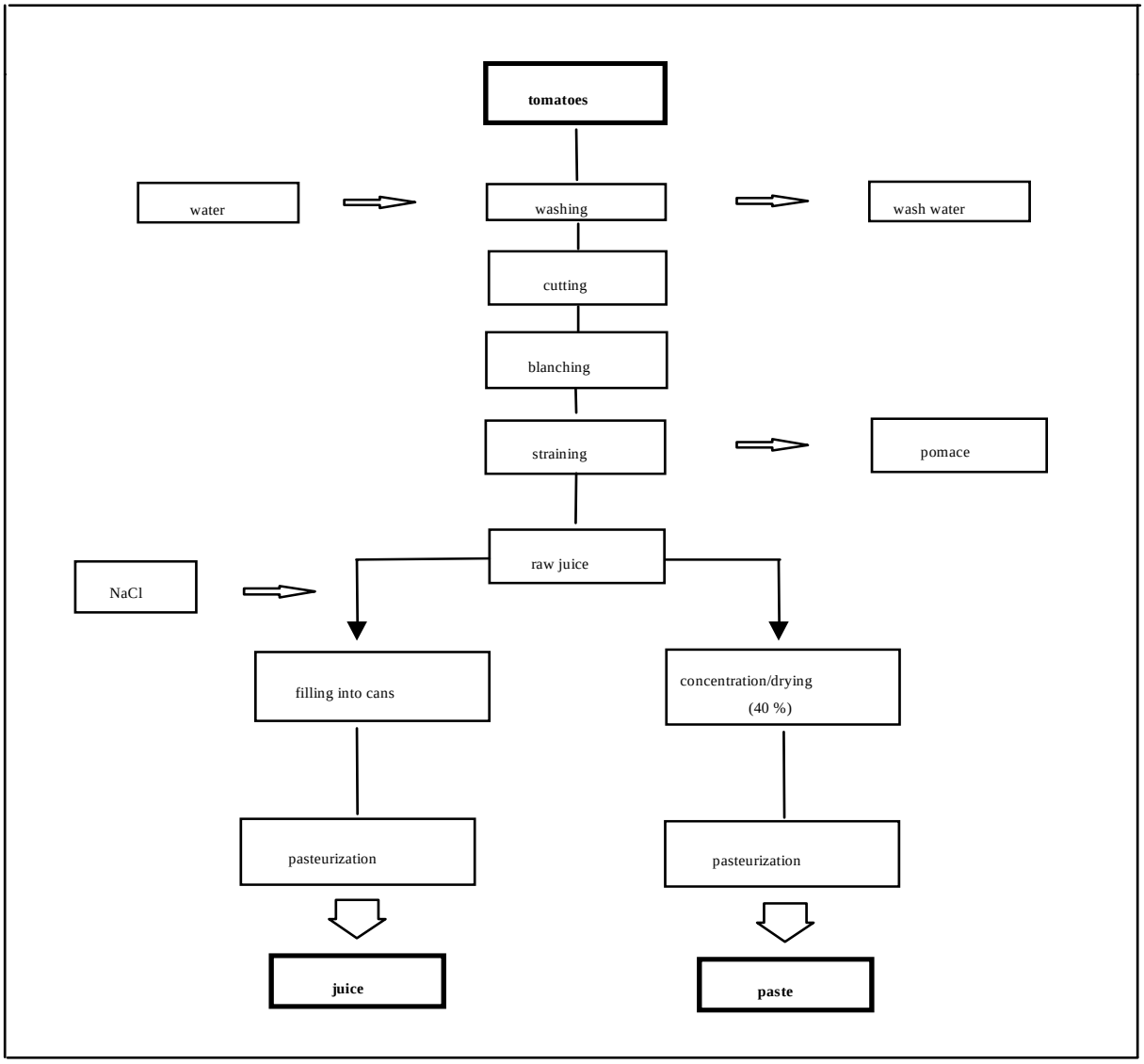
Country	Sample	PHI, days	Residues, mg/kg	Processing factor	*Report no.*, Study no.
Netherlands	fruit	3	0.52	-	*RA-2010/91* 0181-91
	fruit, washed		0.42	0.81	
	preserves		0.19	0.365	
	juice		0.07	0.135	
	paste		1.1	2.1	

Figure 7. Preparation of preserved tomatoes.



bold framed items analysed

Figure 8. Preparation of tomato juice and paste.



Bold framed items analysed

Apples (Tables 44-46). Apples from 4 German residue trials which had been treated 8 times at 0.28 kg ai/ha were sampled at a PHI of 14 days. Bitertanol residues in the raw commodity ranged from 0.08 to 1.0 mg/kg.

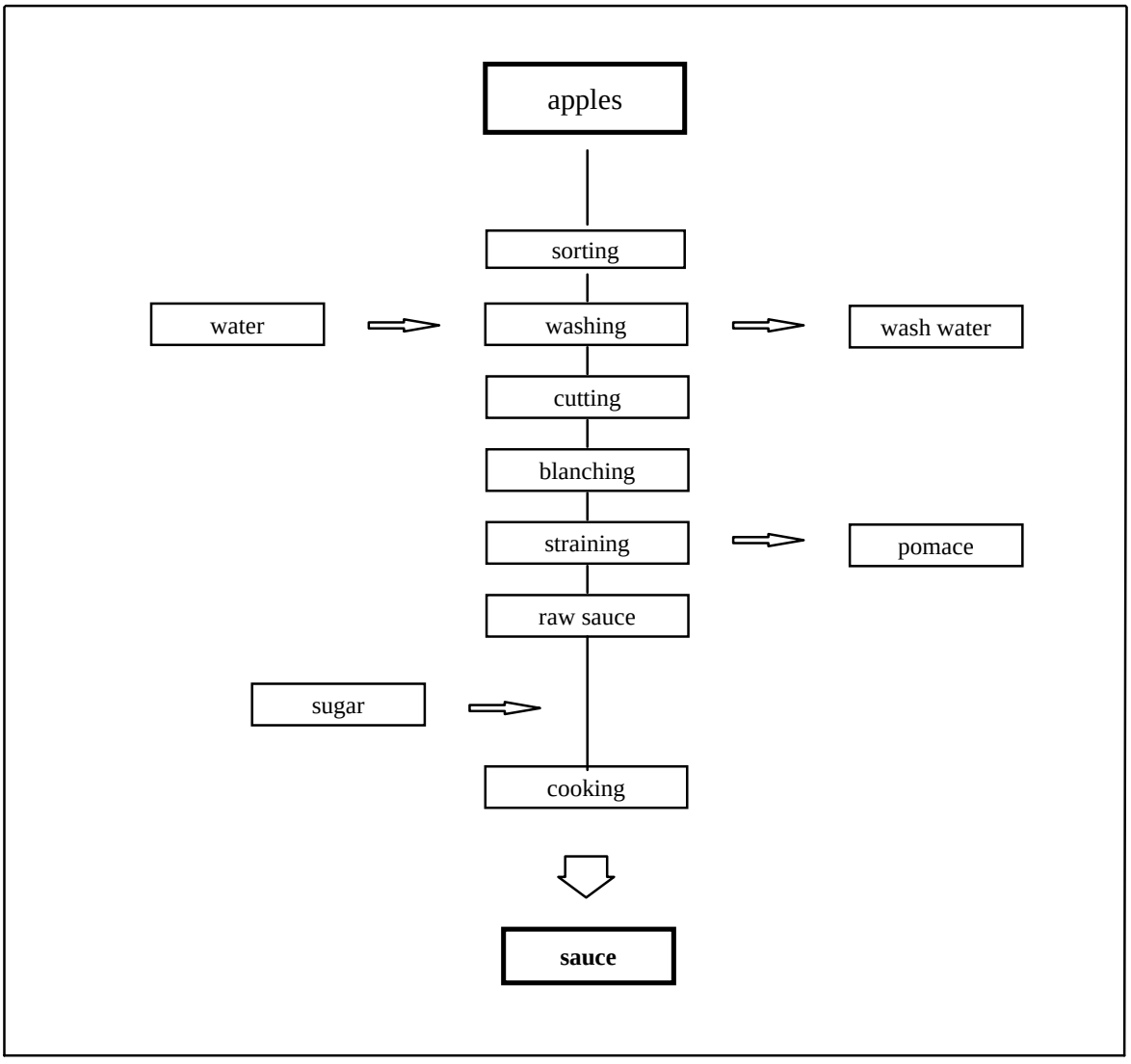
Apple sauce was made according to household procedures and juice by simulated industrial techniques. Apple sauce was prepared by discarding damaged fruit, then washing and cutting the remaining apples, blanching, straining through a sieve and cooking (Figure 9). To prepare apple juice washed apples were pressed to give raw juice, which was then centrifuged and finally pasteurized in an autoclave (Figure 10).

In all 4 studies the residues in apple sauce and juice were either not detectable or below the LOD of 0.02 mg/kg.

Table 44. Bitertanol residues in processed fractions of apples (Germany,1984).

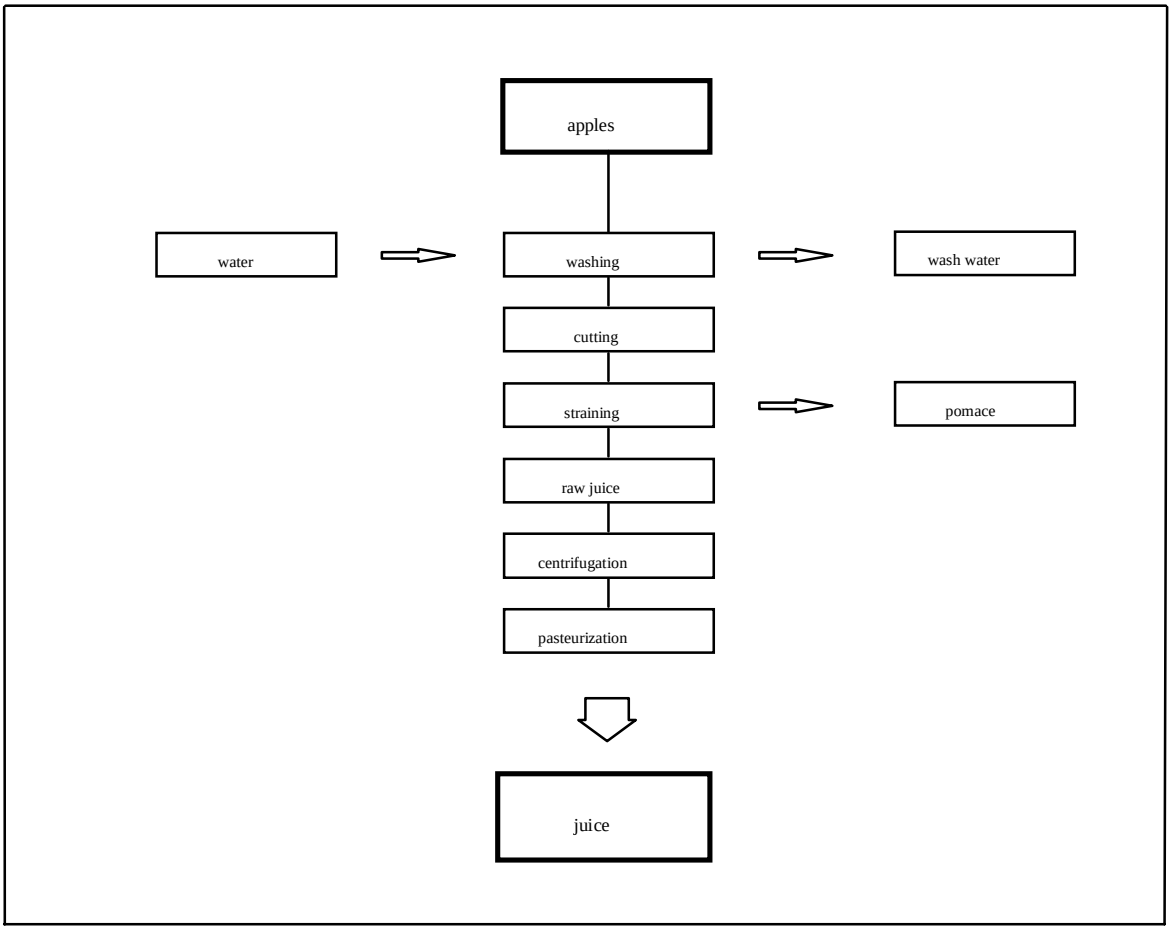
Sample	PHI,days	Residues,mg/kg	Study No.
fruit	14	0.55	10300-84
sauce		<0.02	
juice		<0.02	
fruit	14	0.08	10301-84
sauce		<0.02	
juice		<0.02	
fruit	14	0.23	10302-84
sauce		<0.02	
juice		<0.02	
fruit	14	1.0	10303-84
sauce		<0.02	
juice		<0.02	

Figure 9: Processing of apples to sauce.



bold framed products = residue samples

Figure 10. Preparation of apple juice.



Sandie and Thornton, 1984. As pomace is used for animal feed a study was carried out to determine whether residues were concentrated in it. Ripe apples were sprayed to run-off with bitertanol in the laboratory three times at 0.2 kg ai/hl during of 1 day. This procedure was substituted for spraying in the field because the metabolism study by Puhl and Hurley (1981a) showed that there is very little penetration of bitertanol into the pulp of apples and very little metabolism.

The apples were processed under simulated commercial conditions. Unwashed apples (17 kg) were chopped and pressings into 8 “cheeses” in a small-scale commercial hydraulic apple press. Juice from the eight pressings was pooled and mixed well to suspend the solids. The wet pomace was dried in a forced-draught oven at 77°C for 6.5 hours. The yields and residues of all fractions are shown in Table 45.

Table 45. Bitertanol residues in apples and processed products.

Sample	Residues, mg/kg	Processing factor	Yield, kg	Report no.
Whole fruit, control (chopped)	<0.01		16	86466
Whole fruit, treated (chopped)	8.2		14	
Juice, control	<0.01		7.8	
Juice, treated	0.84	0.1	8.3	
Wet pomace, control	<0.05		6.7	
Wet pomace, treated	21	2.6	5.2	
Dry pomace, control	<0.05		1.9	
Dry pomace, treated	61	7.4	1.6	

Mobay Chemical Corporation, 1985. Apple trees were sprayed with 15 x 1.1 kg ai/ha in Kansas City, Missouri (USA). The processing procedure was similar to that of Sandie and Thornton (1984) except that the pomace was not dried. The results are shown in Table 46.

Table 46. Bitertanol residues in apples and processed products.

Sample	Residues, mg/kg	Processing factor	Report no.
Whole fruit, control	<0.01		87036
Whole fruit, treated	0.49		
Juice, control	<0.01		
Juice, treated	0.09	0.18	
Wet pomace, control	<0.01		
Wet pomace, treated	1.37	2.8	

Cherries (Table 47). Sour cherries were processed into preserved fruit and juice, and jam (2 trials) or pomace (1 trial) in Germany. The trees were treated five times at either 0.38 or 0.56 kg ai/ha. The samples used for processing were collected at a PHI of 21 days and contained residues of 0.36-0.52 mg/kg.

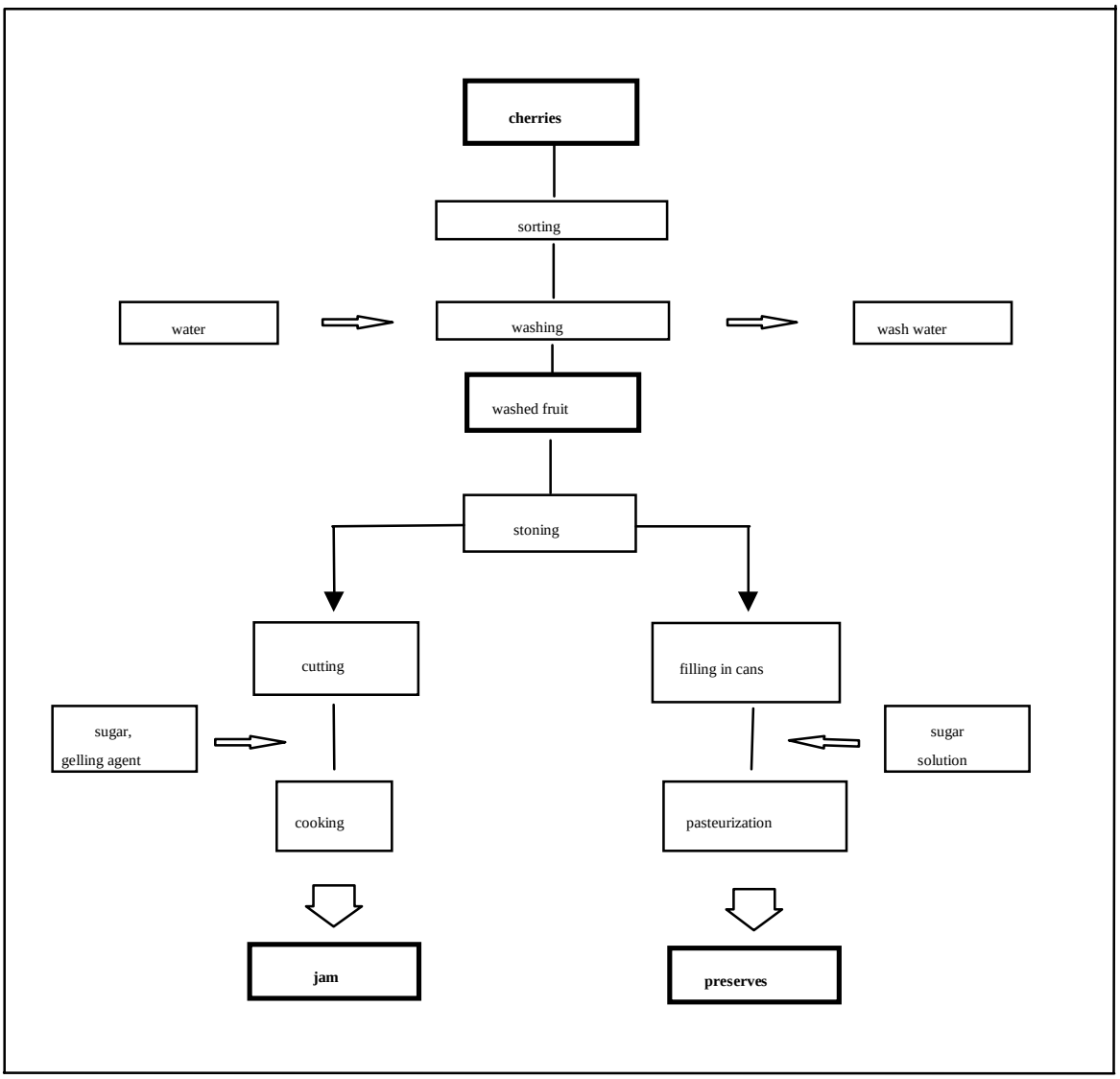
Jam was made by household methods, and preserved fruit and juice by simulated industrial procedures (Figures 11 and 12). The first steps in both processes were discarding damaged fruit, washing, and stoning. Jam was cooked by adding sugar and gelling agent to the chopped fruit and slowly bringing to the boil. Preserves were produced by adding sugar solution to stoned cherries and pasteurizing the canned mixture in an autoclave. Juice was prepared by pressing in a high-pressure press and pasteurizing the juice. The preparation of juice also yielded pomace.

Bitertanol residues in washed and preserved cherries were somewhat lower than in the raw agricultural commodity, were markedly reduced in jam and juice, and hardly changed in pomace.

Table 47. Bitertanol residues in cherries and processed products (Germany, 1986-89).

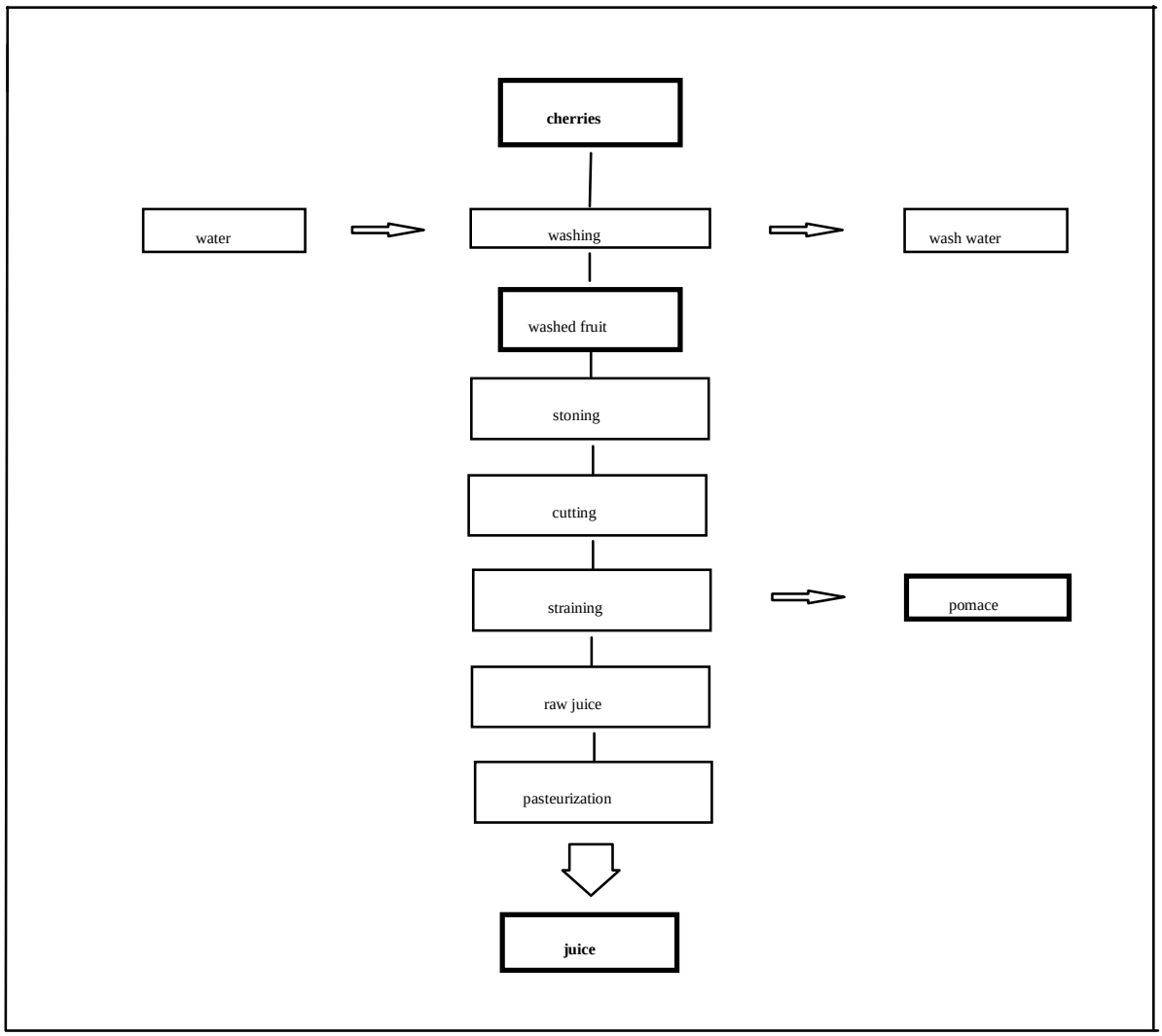
Sample	PHI, days	Residues, mg/kg	Processing factor	Study no.
Fruit	21	0.48	-	10312-86
Fruit, washed		0.44	0.92	
Preserve		0.33	0.68	
Jam		0.26	0.54	
Juice		0.18	0.375	
Fruit	21	0.52	-	10314-87
Fruit, washed		0.39	0.75	
Preserve		0.26	0.5	
Juice		0.06	0.115	
Pomace		0.56	1.1	
Fruit	21	0.36	-	0210-89
Preserve		0.21	0.58	
Jam		0.13	0.36	
Juice		0.01	0.028	

Figure 11. Processing of cherries to jam and preserved fruit.



Bold framed items analysed

Figure 12. Processing of cherries to juice and pomace.



Bold framed items analysed

Peaches (Table 48). Samples from 2 Spanish residue trials with 3 treatments at 0.25-0.61 kg ai/ha (0.038 kg ai/hl) and a PHI of 14 days, containing residues of 0.19 and 0.23 mg/kg, were processed into jam, preserved peaches and juice (Figures 13 and 14). Jam was prepared by domestic methods, and preserves and juice by simulated industrial procedures on a laboratory scale. In both cases, peaches were washed, peeled (except for juice preparation) stoned and cut into pieces. Jam was made by mashing the fruit pieces, adding sugar and gelling agent, and cooking the mixture. Preserves were produced by transferring fruit halves together with a hot sugar solution into cans and pasteurizing them in an autoclave, and peach juice by pressing the fruit pieces in a high-pressure press and pasteurizing the centrifuged raw juice.

No residues above the LOD of 0.02 mg/kg were found in jam or preserves. The residue in the juice was 0.03 mg/kg in both studies. There was thus a considerable decrease of residues in the processed commodities.

The higher residues in washed than in unwashed fruit were not considered to indicate a true increase. A more likely explanation is that the unwashed and washed peaches were from different portions of the field sample.

Table 48. Bitertanol residues in peaches and processed fractions (Spain, 1994).

Sample	PHI, days	Residues, mg/kg	Processing factor	*Report no.* Study no.
fruit	14	0.19	-	*RA-2083/94*
Fruit, washed		0.3	not calculated[1]	0342-94
jam		<0.02		
preserve		<0.02		
juice		0.03		
fruit	14	0.23	-	*RA-2083/94*
Fruit, washed		0.36	not calculated[1]	0343-94
jam		<0.02		
preserve		<0.02		
juice		0.03		

[1] not calculated because of aberrant relation between residues in washed and unwashed peaches (see text)

Figure 13. Processing of peaches to jam and preserved fruit.

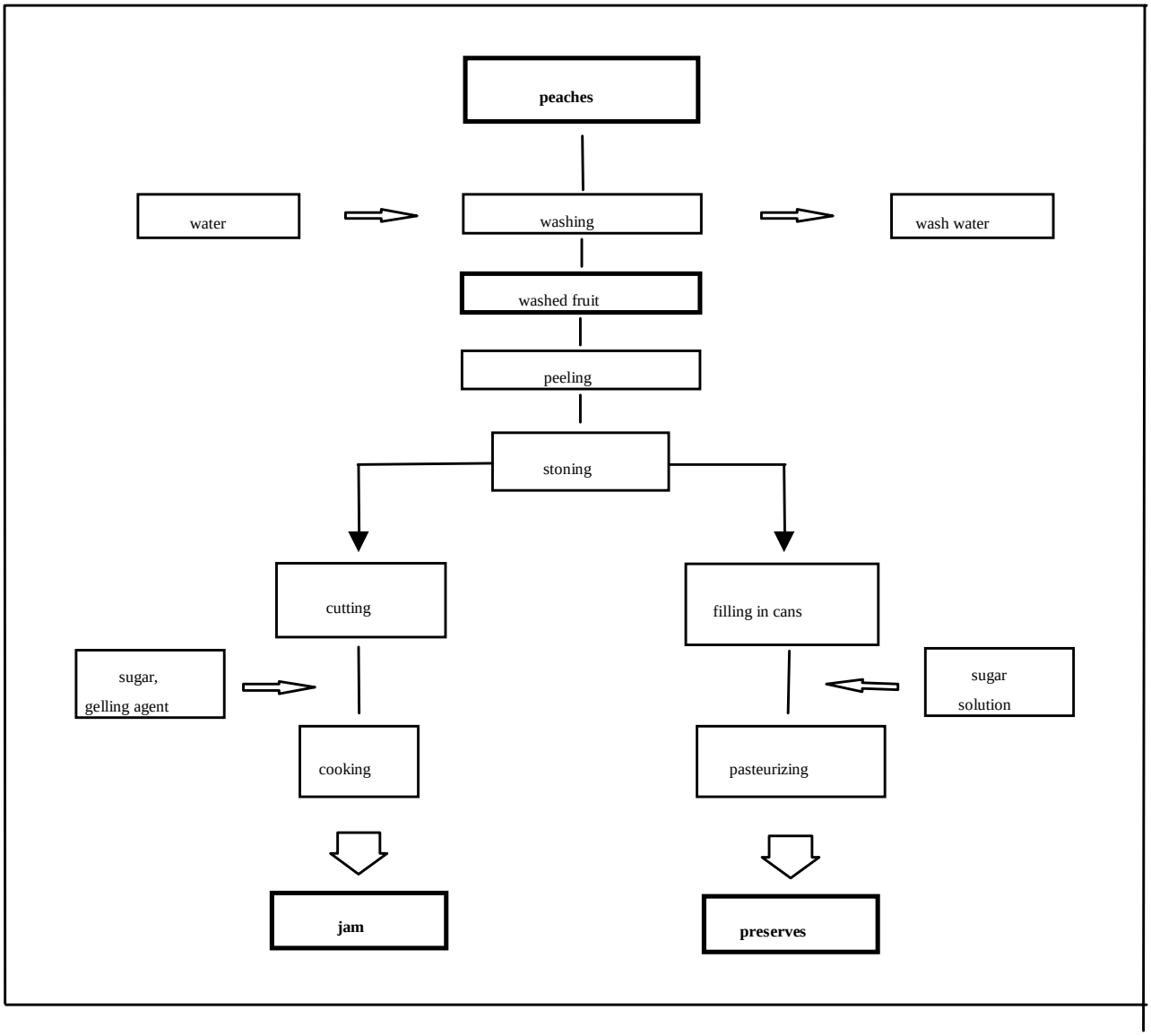
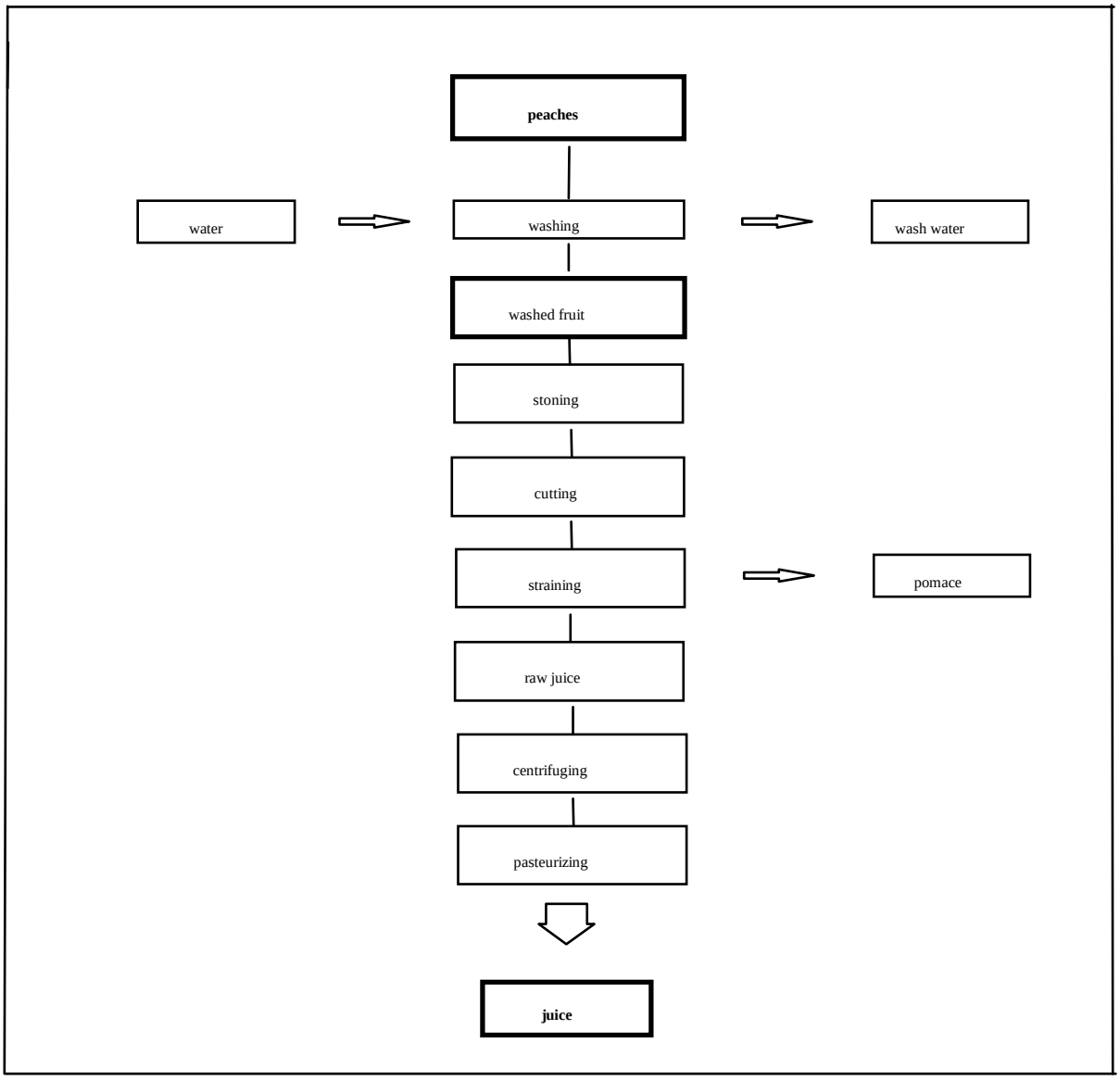


Figure 14. Processing of peaches to juice.



Plums (Table 49). A processing study was included in 2 residues trials on plums in Germany. The plum trees were treated 5 times with bitertanol at 0.38 kg ai/ha (0.025 kg ai/hl). At a PHI of 21 days the residues were 0.21 and 0.22 mg/kg.

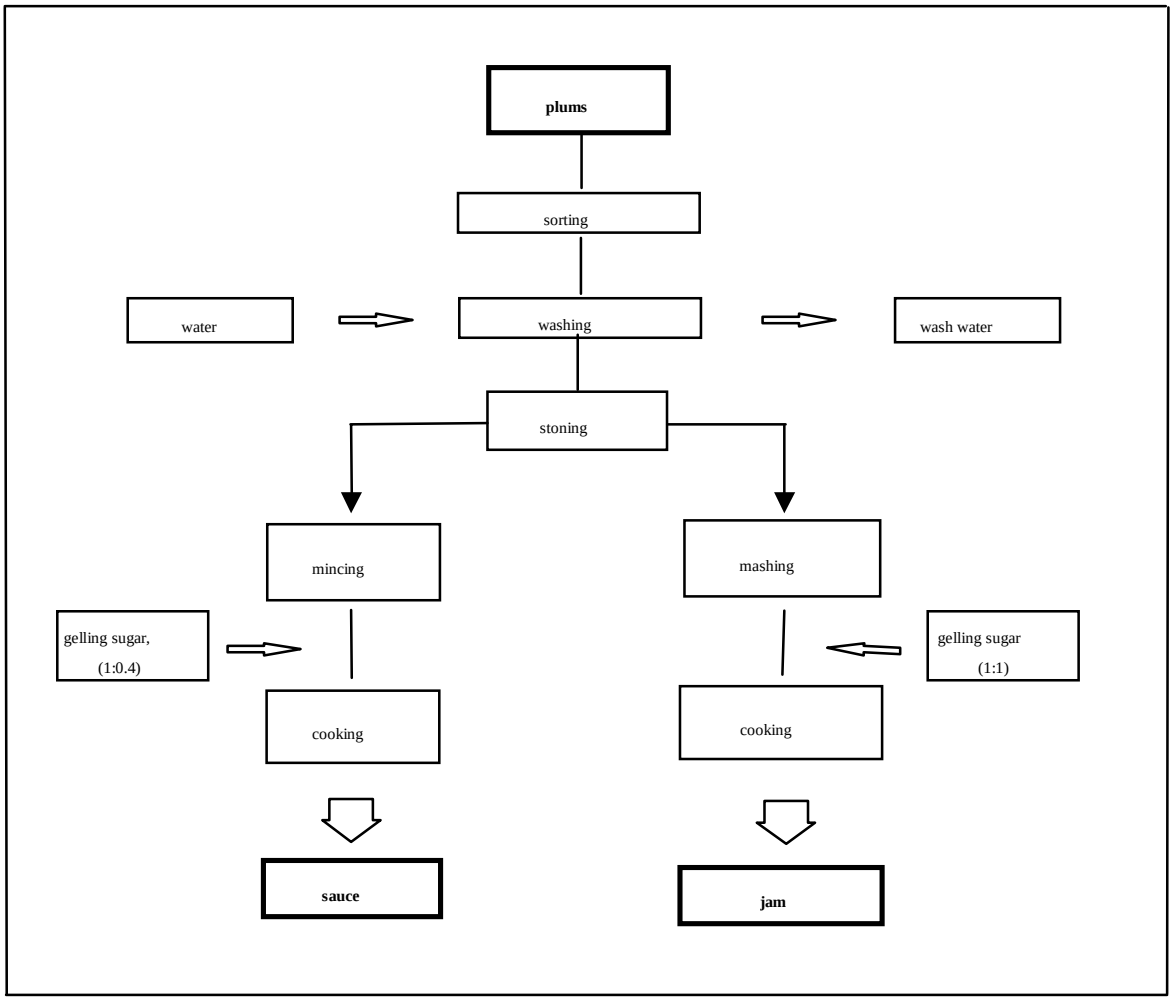
Plum sauce was made in 1 trial and jam in both trials by household methods (Figure 15). Damaged plums were discarded and the others were washed and stoned. Plum sauce was prepared by putting the plums through a mincer, adding gelling sugar (1:0.4), and cooking. Jam was produced by mashing the plums, adding gelling sugar (1:1), and cooking the mixture.

The bitertanol residue in plum sauce was about the same as in the raw plums, and the residues in the jam were about half those in the raw commodity.

Table 49. Bitertanol residues in plums and processed fractions (Germany, 1988).

Sample	PHI, days	Residues, mg/kg	Processing factor	Study no.
Fruit	21	0.22	-	0230-88
Jam		0.14	0.64	
Fruit	21	0.21	-	0232-88
Sauce		0.22	1	
Jam		0.12	0.57	

Figure 15. Preparation of plum sauce and jam.



Residues in the edible portion of food commodities

Apart from the processing studies the only information was on banana pulp, recorded in the section on supervised trials (Table 31).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Information on bitertanol residues in food in commerce in The Netherlands 1994-1996 (Table 50) and 1997 (Table 51) was submitted (Olthof, 1999b).

Table 50. Residues of bitertanol in food in commerce, The Netherlands 1994-1996.

Product	Samples analysed	Samples without residues[1]	Samples with residues below MRL	Samples with residues above MRL	Residues above MRL, mg/kg	MRL, mg/kg
Apples	1654	1653	1	-	-	1
Pears	447	445	2	-	-	1
Peaches	283	282	-	1	0.08	0.05*
Cucumbers	1089	1087	2	-	-	1
Peppers, sweet	1655	1635	20	-	-	1
Tomatoes	1242	1213	29	-	-	1
Celery	300	298	1	1	1.4	0.05*
Other arable products	759	758	-	1	0.91	0.05*

[1]LOD = 0.05 mg/kg

Table 51. Residues of bitertanol in food in commerce, The Netherlands 1997.

Product	Samples analysed	Samples without residues[1]	Samples with residues below MRL	Samples with residues above MRL	Residues above MRL, mg/kg	MRL, mg/kg
Pears	90	89	1	-	-	1
Peaches	39	37	-	2	0.39, 0.55	0.05*
Nectarines	65	64	-	1	0.31	0.05*
Currants (black, red and white)	142	141	-	1	0.07	0.05*
Peppers, sweet	605	602	3	-	-	1
Courgettes	79	78	1	-	-	1
Beans (with pods)	262	261	-	1	0.25	0.05*

[1]LOD = 0.05 mg/kg

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country/Commodity	MRL, mg/kg	Notes
Argentina		
Apple	1	
Banana	0.5	
Peanut	0.2	
Australia		
Apple	1	
Beans, except Broad bean and Soya bean	0.3	
Bean, Broad (green pods and/or immature seeds)	0.3	
Cereals, forage	0.1	
Cereals, grain	0.05	Level at or about the LOD
Eggs	0.01	Level at or about the LOD
Meat, Mammalian	0.2	
Edible offal, Mammalian	1	
Meat, fat	1	
Milks, fat	2	
Peanut	0.2	Level at or about the LOD
Peanut fodder	100	
Peanut forage	100	
Poultry meat	0.2	
Poultry, Edible offal of	1	
Pulses	0.3	
Austria		

Country/Commodity	MRL, mg/kg	Notes
Beet, Sugar	0.2	
Cereals	0.1	
Other plant commodities	0.05	
Pome fruit	1	
Belgium		
Cherry, sweet	0.3	
Cucumber	0.3	
Gherkin	0.3	
Other plant commodities	0	Below the LOD (0.05 mg/kg)
Pome fruit	0.3	
Strawberry	0.3	
Tomato	1	
Brazil		
Apple	1	
Bean	0.1	
Peanut	0.2	
Denmark		
Apple	2	
Cherry	2	
Pear	2	
Finland		
Apple	1	
France		
Apricot	1	
Beet, Sugar	0.05	T
Beet, Sugar, leaf	0.05	T
Peach	1	
Plum	1	
Pome fruit	1	
Germany		
Banana	0.5	
Bean, pods and/or immature seeds	0.5	
Cereals	0.1	
Cucumber	0.5	
Other plant commodities	0.05	
Pome fruit	2	
Stone fruit	2	
India		
Tea	5	
Israel		
Almond	1	
Apple	1	
Loquat	2	
Pear	1	
Plum	2	
Italy		
Almond	1	
Bean, without pod	0.5	
Beet, Sugar	0.5	
Cucumber	0.5	
Leek	0.5	
Pome fruit	1	
Stone fruit	1	
Wheat	0.02	
Zucchini	0.5	
Japan		
Apple	0.6	
Apricot	2	
Apricot, Japanese	2	
Banana	0.5	
Barley	0.05	
Bean, Adzuki	0.2	

Country/Commodity	MRL, mg/kg	Notes
Bean, Broad	0.2	
Bean, Kidney (pods and/or immature seeds)	0.3	
Beet, Sugar	0.5	
Buckwheat, Common	0.05	
Cherry	3	
Cucumber	0.5	
Loquat	0.6	
Maize/Corn	0.05	
Melon	1	
Other cereals	0.1	
Other pulses	0.2	
Pea, Garden	0.2	
Peach	1	
Peanut	0.1	
Pear	0.6	
Pear, Oriental	0.6	
Plum	1	
Quince	0.6	
Rye	0.1	
Soya	0.2	
Strawberry	1	
Wheat	0.1	
Luxembourg		
Cherry, Sour	0.3	
Cucumber	0.3	
Gherkin	0.3	
Other plant commodities	0.05	LOD
Pome fruit	0.3	
Malaysia		
Apple	1	
Banana	0.5	
Peanut	0.2	
Pear	1	
Mexico		
Bean	0.05	
Cotton	1	
Netherlands		
Blackberry	0.05	Level at or about the LOD
Cereals	0.05	Level at or about the LOD
Cherry	1	
Fruiting vegetables	1	
Other plant commodities	0	Below the LOD (0.05 mg/kg)
Pome fruit	0.1	
New Zealand		
Pome fruit	1	
Poland		
Banana	0.5	
Pome fruits	1	
Stone fruits	2	
Fruits except as otherwise listed	0.2	
Cereal grains	0.1	
South Africa		
Apple	1	
Apple	0.05	E
Apricot	0.5	
Apricot	0.05	E
Bean	0.1	
Nectarine	0.5	
Nectarine	0.05	E
Peach	0.5	
Peach	0.05	E
Peanut, shelled	0.05	

Country/Commodity	MRL, mg/kg	Notes
Pear	1	
Pear	0.05	E
Plum	0.5	
Plum	0.05	E
South Korea		
Apple	0.6	
Apricot	1	
Apricot, Japanese	2	
Banana	0.5	
Barley	0.05	
Bean, Adzuki	0.2	
Bean, Broad	0.2	
Bean, Kidney	0.2	
Bean, Mung	0.2	
Buckwheat, Common	0.1	
Cherry	2	
Cucumber	0.5	
Maize/Corn	0.05	
Millet, French	0.1	
Oats	0.1	
Other pulses	0.2	
Pea	0.2	
Peach	1	
Peanut	0.1	
Pear	0.6	
Plum	1	
Quince	0.6	
Rye	0.1	
Sorghum, grain	0.1	
Soya	0.2	
Strawberry	1	
Wheat	0.1	
Spain		
Beet, Sugar	0.05	
Berries and small fruit	0.05	
Cacao	0.05	
Cereals	0.05	
Citrus fruit	0.05	
Coffee	0.05	
Cola	0.05	
Forage crops and straw	0.05	
Fruit and vegetables, dried	0.05	
Hops	0.05	
Nuts	0.05	
Oil plants, seed	0.05	
Pome fruit	1	
Potato	0.05	
Pulses	0.05	
Spices	0.05	
Stone fruit	1	
Sugar cane	0.05	
Tea	0.05	
Tobacco	0.05	
Tropical. and subtropical fruits	0.05	
Vegetables	0.05	
Switzerland		
Cereals	0.05	
Pome fruit	0.6	
Stone fruit	0.6	
Taiwan		
Banana	1	
Peanut	0.1	

Country/Commodity	MRL, mg/kg	Notes
Pome fruit	0.5	
UK		
Apple	1	
Apricot	1	
Banana	0.5	
Nectarine	1	
Other pome fruit	1	
Peach	1	
Pear	1	
Plum	1	
Quince	1	
Uruguay		
Apple	2	
USA		
Banana, whole fruit	0.2	I
Venezuela		
Banana	0.1	
Bean	0.1	
Bean, Broad	0.1	
Cacao	0.1	
Peach	0.1	
Peanut	0.2	
Plantain	0.1	
Soya	0.1	
Strawberry	0.1	
Vegetables	0.1	

T: temporary tolerance
I: import tolerance
E: export tolerance
LOD: limit of determination

APPRAISAL

Bitertanol, 1-(biphenyl-4-yloxy)-3,3-dimethyl-1-(1*H*-1,2,4-triazol-1-yl)butan-2-ol (2 diastereo-isomers), is an effective fungicide used as a foliar spray on fruits and vegetables and as a seed treatment for cereals for certain diseases. The compound was originally evaluated for residues in 1984 when TMRLs were recommended for a number of commodities. The fungicide was evaluated under the CCPR Periodic Review Programme in 1998 for toxicology and by the present Meeting for residues.

The Meeting received information on animal and plant metabolism, environmental fate, analytical methods, updated GAP, supervised trials on crops, animal feeding studies and the effects of processing on residues.

Metabolism and environmental fate

In animal metabolism studies, the compound was uniformly-labelled with ^{14}C in the phenyl ring remote from the oxygen. The absorption, distribution, metabolism and excretion of [^{14}C]bitertanol has been studied in rats, cows and hens.

Bitertanol is rapidly absorbed from the intestinal lumen, and is readily distributed within the body. The excretion of the parent compound and its biotransformation products is fast (in rats almost complete within 72 h) and occurs mainly in the faeces (about 90%) by biliary excretion, owing to the lipophilic nature of the compound.

The main metabolic reactions are hydroxylation of the phenyl ring in the *para* position and oxidation of the *tert*-butyl moiety to form bitertanol alcohol and the corresponding carboxylic acid. There is no significant difference between the metabolism in rats, cows and poultry. Unchanged bitertanol and its *para*-hydroxylated metabolite in free and conjugated form were the main residues in the edible tissues and eggs of poultry (75-92% and 81-83% of the total ^{14}C respectively), and in the edible tissues and milk of the dairy cow (23-51% and 84% of the total ^{14}C respectively).

Plant metabolism studies were carried out with biphenyl- and triazole-labelled bitertanol on apples, peanuts, cotton (foliar spray treatment) and wheat (seed treatment).

Bitertanol was metabolised slowly in the investigated crop species after foliar spray application (half-lives 141 days in peanuts, 150 days in apples). Unchanged bitertanol was the main residue in apple fruits (83% of the biphenyl label, 96% of the triazole label), peanut shoots (86% of the total ^{14}C) and cotton plants (79% of the total ^{14}C). Oxidation of the hydroxyl group yields the keto analogue (BUE 1662) and oxidative cleavage of the biphenyl moiety yields bitertanol benzoic acid (BUE 2684). The compound is also conjugated at the free hydroxyl group to form a malonyl glucoside.

After seed treatment of wheat at a commercial application rate, the metabolites detected at harvest in the grain from the triazole label were derivatives of 1,2,4-triazole: triazolylalanine (50–66% of the total ^{14}C, 0.12–0.16 mg/kg) and triazolylacetic acid (22–34% of the total ^{14}C, 0.04–0.07 mg/kg). The parent compound was not detectable.

The degradation of bitertanol does not lead to environmentally significant levels of degradation products in soil or water.

The degradation of bitertanol in soil was comparable in all the studies. It was quickly degraded (half-life <1 to 9 days). At the end of the test period the degradation curve flattened, so the DT-90 value was 15 to 102 days depending on the soil type. The main degradation product was CO_2 (50-64% of the applied ^{14}C). Owing to the rapid degradation only small amounts of intermediate products were detected. Bitertanol benzoic acid (BUE 2684) represented less than 0.3% of the applied ^{14}C; no other degradation products were identified. The unidentified compounds in the extracts represented $\leq$4.2% of the applied ^{14}C. Unextractable residues, which were bound to the stable humin fraction, increased within the first 22 days up to 30-50% of the applied ^{14}C, then decreased while mineralisation continued.

Aged bitertanol residues exhibit only a very low mobility in soil. In BBA standard soil 2.1 which showed the highest mobility the TRR in the leachate at 22°C and after 30 days of ageing was 0.5–1% of the applied radioactivity after 48 h rainfall, indicating that the leaching potential is negligible, which would be expected from the strong adsorption to the soil matrix. Photolysis on soil surfaces plays a minor role in the environmental destruction of the compound.

Bitertanol is stable to hydrolysis in aqueous solutions but it can easily be degraded by light owing to the chromophoric biphenyl moiety. However the photolytic effect might be of little significance under environmental conditions since only little light of the relevant wavelengths (<290 nm) penetrates water.

In water/sediment systems a high proportion of the applied radioactivity was transported into the sediment, reaching a maximum of 69-91% after 25 days. This decreased to 38-44% of the applied ^{14}C at the end of the test period of 120 days. Only 2-3% of the applied ^{14}C was identified as the parent compound in the surface water after 53 days. In the sediment extracts 24-59% of the applied ^{14}C was identified as bitertanol at 53 days, decreasing to 3-4% at 120 days. The mineralization rate is high and intermediate products are found only in trace amounts.

Residues in rotational crops were determined in kale, mustard, sugar beet, and wheat planted in the soil 31, 118 and 364 days after treatment (DAT) of the target crop of peanuts with biphenyl-labelled bitertanol eight times at 0.56 kg ai/ha as a foliar spray. Total radioactive residues in harvested samples ranged from 0.1 mg/kg (118 DAT) to 0.02 mg/kg (364 DAT) in leafy vegetables (kale, mustard), from 0.38 mg/kg (118 DAT) to 0.01 mg/kg (364 DAT) in sugar beet roots, and from 0.23 (31 DAT) to 0.01 mg/kg (364 DAT) in wheat ears.

No information was reported on the fate of the 1,2,4-triazole moiety in succeeding crops.

Methods of residue analysis

Residue analytical methods for bitertanol *per se* in plant and animal products are based on extraction with acetone/water, clean-up by liquid-liquid partition with dichloromethane, and purification of the organic phase by gel permeation chromatography. Bitertanol is determined by gas chromatography using a nitrogen-selective thermionic detector. This method has been modified in the clean-up procedures (e.g. by the use of Chem-Elut). Validation for plant and animal commodities showed recoveries of about 70-110%. The typical limits of determination in plant materials and animal products are 0.01- 0.05 mg/kg.

The analytical method provided by The Netherlands is based on a similar extraction. There is no clean-up for plant materials but animal products are cleaned up by gel permeation chromatography (GPC), HPLC or liquid-liquid partitioning (LLP). Determination is carried out by gas chromatography with an ion trap detector or nitrogen-phosphorus detector (NPD). The LOD was reported as 0.05 mg/kg for non-fatty and fatty foods and recoveries were generally between 90 and 100%.

A method was developed to quantify bitertanol and its metabolites ("total bitertanol") in bovine and poultry tissues, milk and eggs. Extraction was with various solvents (acetone, methanol, hexane), depending on the sample, and the extracts were acid-hydrolysed to release 1,2,4-triazole. The 1,2,4-triazole was derivatized to form triazolylpinacolone which was determined by gas chromatography using a thermionic nitrogen detector. Several clean-up steps were required including partitioning, ion exchange chromatography and high performance liquid chromatography. Recoveries were determined at 0.05 mg/kg and 0.1 mg/kg from all samples and additionally at 0.5 mg/kg and 2 mg/kg from bovine liver. The recoveries were between 60 and 120%.

For the enforcement determination of bitertanol in ground and drinking water a thin-layer separation with UV detection, based on automated multiple development (AMD), was developed. Recoveries were between 85 and 116%, and the LOD was 0.05 µg/l.

Information was submitted on the stability of bitertanol residues in various stored analytical samples. The Meeting concluded that the compound was stable for the duration of the studies (at least 3.5 years in apples, 2 years in cherries and peaches, 1 year in green and dry beans and 2 years in bovine tissues).

Definition of the residue

On the evidence of studies with foliar spray treatments of apples, cotton and peanuts, the residue of concern was bitertanol *per se*.

After seed treatment of wheat at a commercial application rate, the metabolites detected at harvest in the grain from the triazole label were conjugates of 1,2,4-triazole: triazolylalanine (50–66% of the total ^{14}C) and triazolylacetic acid (22–34% of the total ^{14}C). Neither the parent nor free 1,2,4-triazole were detectable.

As 1,2,4-triazolylalanine can arise as a plant metabolite of several pesticides that contain a 1,2,4-triazole moiety, being formed by the conjugation of the latter with serine, it was evaluated by

the 1989 JMPR for toxicology and residues. A biotransformation study on rats showed that 1,2,4-triazolylalanine is rapidly absorbed and excreted, mainly as the unchanged compound in the urine. The 1989 Meeting concluded that residues of 1,2,4-triazolylalanine arising from the use of triazole fungicides do not present a toxicological hazard.

The animal metabolism studies on rats, a cow and laying hens indicate that the parent compound bitertanol and the metabolite *p*-hydroxybitertanol (free and conjugated) are the main residue components in animal tissues, milk and eggs.

As bitertanol has no acidic or basic properties in aqueous solution, the partition coefficient will not be influenced by the pH. The octanol-water partition coefficients (log P_{OW} = 4.04 diastereomer A, 4.15 diastereomer B) indicate that bitertanol is fat-soluble.

The Meeting concluded that the following residue definitions are appropriate.

For compliance with MRLs. For plant and animal products: bitertanol.

For estimations of dietary intake. For plant products: bitertanol. For animal products: sum of bitertanol, *p*-hydroxybitertanol and the acid-hydrolysable conjugates of *p*-hydroxybitertanol.

Residues resulting from supervised trials

Information was reported to the Meeting on registered uses of bitertanol and on supervised residue trials on apples, cherries, plums, nectarines, peaches, bananas, tomatoes, cucumbers, barley, oats, rye, wheat, cereal fodder and forage. Most trials were carried out in Europe. It was assumed that for the conduct of residue trials the European climatic conditions and weather influences could be divided into two regions.

Northern and central Europe: Sweden, Norway, Denmark, the UK, Ireland, northern and central France, Belgium, The Netherlands, Germany, Poland.
Southern Europe and the Mediterranean: Spain, Portugal, southern France, Italy, Greece.

Pome fruits. Trials on apples were reported from France, Germany, Italy, Spain and South Africa and on pears from Germany. French and Greek GAP for the use of bitertanol on pome fruit call for a spray concentration of 0.025 kg ai/hl with a PHI of 14 days for preventive and curative treatments. The labels recommend 2 applications with an interval of 1 week for curative treatments followed by preventive sprayings every 10-14 days. The labels also require an increase in concentration of the pesticide if the spray volume is reduced.

Twelve German trials on apples were carried out according to French and Greek GAP (8-12 x 0.025 kg ai/hl, PHI 14 days). These trials, which can also be used to represent the residue situation in Northern France, gave residues in rank order of 0.08, 0.09, 0.13, 0.13, 0.23, 0.25, 0.55, 0.62, 0.7, 0.86, 1.0 and 1.8 mg/kg.

In the 7 Southern European apple trials (1 in Spain according to Spanish GAP; 2 in Spain, 3 in Italy and 1 in France according to French GAP) the residues after 5 applications were 0.08, 0.09, 0.18, 0.23, 0.24, 0.34 and 0.36 mg/kg.

Current GAP for South Africa includes 1 or 2 treatments at 0.008 kg ai/hl with a PHI of 14 days, but the 9 apple trials reported were at higher rates (6-7 x 0.013–0.025 kg ai/hl). The residues were from 0.25 to 0.71 mg/kg.

In summary, the bitertanol residues in apples from trials according to French, Spanish and Italian GAP in rank order (median underlined) were 0.08, 0.08, 0.09, 0.09, 0.13, 0.13, 0.18, 0.23, 0.23, 0.24, 0.25, 0.34, 0.36, 0.55, 0.62, 0.7, 0.86, 1.0 and 1.8 mg/kg.

Twelve German trials on pears were carried out according to the German registered application rate (0.0125 kg ai/hl), but the number of treatments was 12 instead of the 5 specified on the label. The residues at the GAP PHI of 14 days in rank order were 0.22, 0.23, 0.25, 0.33, 0.63, 0.65, 0.91, 0.92, 0.92, 0.93, 0.97 and 1.1 mg/kg. The Meeting noted that higher residues could occur in pears than in apples from the same application rate.

The Meeting agreed to recommend maintaining the CXL of 2 mg/kg for pome fruits. An STMR of 0.24 mg/kg was estimated for pome fruits on the basis of the residues found in apples.

Stone fruits

The residues from trials carried out before 1996 were mainly reported for fruit without stones, but from trials in 1996 as fruit including stones. The Meeting was informed that the stone represents about 10% of the whole fruit weight and agreed to combine the data on fruit with and without stones.

Cherries. Residue trials were conducted in Germany and France. The trials in Germany were evaluated against German GAP (3 x 0.038 kg ai/hl, PHI 21 days), and the trials in southern France against Greek GAP (0.025-0.038 kg ai/hl, PHI 10 days). The samples from the southern French trials were analysed including the stones, but the residues from Germany were reported for fruit without stones, although the residue in the whole fruit was calculated in 2 trials, where the fruit pulp represented 82–92% (mean 87.6%) of the whole fruit weight.

Of the 14 German trials on sour cherries, 6 trials with 3–4 treatments after flowering with 0.038 kg ai/hl (+ 34%) and a PHI of 21 days complied with GAP. The remaining 8 trials were with 5 treatments after flowering or no sample was taken at the recommended PHI. The results showed residues in fruits without stones of 0.19, 0.36, 0.52, 0.68, 0.83 and 0.85 mg/kg.

In 6 French trials sweet cherries were treated twice at 0.03 kg ai/hl. Four of the trials were carried out in southern France and evaluated against Greek GAP. The residues in fruit with stones were 0.08, 0.15, 0.17 and 0.37 mg/kg. The 2 other trials in northern France could not be evaluated against Greek GAP and did not comply with German GAP.

The bitertanol residues in all the evaluated German and French trials in rank order (median underlined) in fruit **without**/with stone were 0.08, 0.15, 0.17, **0.19**/0.17, **0.36**/0.32, 0.37, **0.52**, **0.68**, **0.83** and **0.85** mg/kg. The Meeting estimated an STMR of 0.365 mg/kg and a maximum residue level for bitertanol in cherries of 1 mg/kg to replace the CXL (2 mg/kg).

Plums. Residue trials were carried out in Germany (12), southern France (4) and Portugal (1).

In the German trials, the residues were reported for fruit without stones, but with calculation of the residue in the whole fruit in 4 trials. In the samples at the GAP PHI, the fruit pulp represented 93–95% (mean 94%) of the whole fruit weight. The results of the French trials were also reported for fruit without stones but with calculation of fruit including stone in one trial.

The German trials were evaluated against French GAP (0.02–0.03 kg ai/hl, PHI 14 days, number of preventive, curative and eradicative treatments not specified). Based on a water rate of 1000 and 1500 l/ha, the spray concentration was 0.025 and 0.38 kg ai/hl. The number of treatments after flowering was 3 in 6 trials, 4 in 1 trial and 5 in 5 trials. The residues in rank order in fruit **without**/with stone were **0.04**, **0.15**, **0.16**, **0.19**, **0.21**, **0.33**, **0.58**/0.55, **0.59**, **0.89**/0.85, **0.94**, **1.4**/1.3 and **1.8**/1.7 mg/kg.

Portuguese GAP (2 x 0.02 kg ai/hl, PHI 7 days) was used to evaluate 4 trials in southern France. Fruits **without**/with stones showed residues of **0.09**, **0.34**, **0.36** and **0.49**/0.45 mg/kg.

All results evaluated gave residues in rank order of **0.04**, **0.09**, **0.15**, **0.16**, **0.19**, **0.21**, **0.33**, **0.34**, **0.36**, **0.49**/0.45, **0.58**/0.55, 0.59, **0.89**/0.85, **0.94**, **1.4**/1.3 and **1.8**/1.7 mg/kg.

On the basis of the German and French residue data the Meeting estimated an STMR of 0.35 mg/kg and agreed to recommend maintaining the CXL of 2 mg/kg.

Peaches and nectarines. GAP is the same for nectarines and peaches in southern Europe and South Africa.

Residue trials on nectarines were carried out in Italy (3), southern France (2) and South Africa (3). The Italian and southern French trials with 1-2 x 0.018-0.019 kg ai/hl, PHI 7 days, complied with Portuguese GAP (1-2 x 0.017-0.02 kg ai/hl, PHI 7 days). The residues in fruits without stones were 0.12, 0.13, 0.20, 0.23 and 0.25 mg/kg.

Two of the 3 South African trials on nectarines could not be evaluated because the application rate was twice the rate prescribed by GAP or samples were not taken at the PHI of 35 days. In the third trial conducted according to GAP, the residue in the fruit without stone was 0.1 mg/kg at day 35, but 0.17 mg/kg at day 49.

On peaches, 6 trials were conducted in Spain, 1 in Portugal and 6 in South Africa. The Portuguese and Spanish trials with 3 x 0.03-0.038 kg ai/hl were according to Spanish GAP (1-3 x 0.025-0.038 kg ai/hl, PHI 15 days) and most of them also complied with Greek GAP (0.025-0.038 kg ai/hl, PHI 10 days). The residues in fruit **without**/with stones were **0.05**, **0.10**, **0.26**/0.24, **0.27**/0.26, **0.43**/0.41, **0.54**/0.49, and **0.74**/0.71 mg/kg.

Four of the 6 South African trials on peaches could not be evaluated because the application rate was twice the rate prescribed by GAP or samples were not taken at the PHI of 35 days. In both the 2 trials according to GAP, the residues were 0.12 mg/kg at day 35 in fruit without stones.

Because GAP for nectarines and peaches is the same, a maximum residue level and STMR were estimated from the combined data. All the residues in nectarines and peaches **without**/with stone in rank order were **0.05**, **0.10**, **0.12**, **0.12**, **0.12**, **0.13**, **0.17**, **0.20**, **0.23**, **0.25**, **0.26**/0.24, **0.27**/0.26, **0.43**/0.41, **0.54**/0.49 and **0.74**/0.71 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg (the same as the CXL) and an STMR of 0.20 mg/kg for peaches and nectarines.

Apricots. As no residue data were provided, the Meeting agreed to propose the withdrawal of the CXL of 1 mg/kg.

Bananas. Bitertanol is registered in Belize, Costa Rica, the Dominican Republic, Guatemala, Nicaragua and Panama with application at 0.15 kg ai/ha and 0.5-1.4 kg ai/hl. Further uses are in Honduras (0.15 kg ai/ha, 0.02-0.2 kg ai/hl), Cameroon (0.15 kg ai/ha, 1.5-3 kg ai/hl), Philippines (0.15-0.2 kg ai/ha, 0.5-0.65 kg ai/hl) and Taiwan (0.12 kg ai/ha, 0.4 kg ai/hl). The PHI is either 0 days or not specified. Residue trials were carried out in Costa Rica, Honduras, the Philippines, Taiwan and Cameroon.

Five trials in Costa Rica at 10–16 x 0.12-0.24 kg ai/ha, 0.2-0.25 kg ai/hl could not be evaluated because the interval between the final application and harvest was 4 and 8 days whereas GAP permits a 0-day PHI. The residues in 2 further trials with treatments of 9 x 0.44 kg ai/hl, PHI 3 days (88% of the lowest recommended concentration rate) in the whole fruit/pulp were 0.24/0.11 mg/kg unbagged and 0.03/0.02 mg/kg bagged.

Five trials in Honduras with 12 x 0.69–1.3 kg ai/hl were evaluated as they complied with the GAP of the other Central American countries. On day 0, the residues in the whole fruit/pulp were

0.1/0.04, 0.32/0.13 and 0.06/0.03 mg/kg in unbagged bananas, and 0.02/0.02, 0.03/<0.01 and 0.03/0.02 mg/kg in bagged. Four further trials in Honduras (12 x 0.06 kg ai/hl, PHI 0 days) were according to Honduras GAP (0.02-0.2 kg ai/hl). The residues in the whole fruit/pulp in unbagged bananas were 0.06/0.03 and 0.36/0.17 mg/kg and in bagged bananas 0.06/0.01 and 0.04/0.02 mg/kg.

Four trials were carried out in the Philippines: 2 were at exaggerated rates (10 x 1.25 kg ai/hl) and the others (26 x 0.69–0.87 kg ai/hl) approximated GAP. As the residues were determined in bagged bananas, they were <0.05 mg/kg in fruit, pulp and peel.

The 2 trials in Taiwan (12 x 0.094 kg ai/hl) could not be evaluated because they did not comply with GAP.

The 2 trials in Cameroon could not be evaluated because the intervals between the final applications and harvest were 6 and 12 days whereas Cameroon GAP does not specify a PHI, implying that 0 days is permitted.

In summary, the residues in unbagged whole bananas in trials in accordance with GAP were Costa Rica 0.24 mg/kg, Honduras 0.06, 0.06, 0.1, 0.32 and 0.36 mg/kg. The respective values for bagged bananas were Costa Rica 0.03 mg/kg, Honduras 0.02, 0.03, 0.03, 0.04, 0.06 mg/kg, and the Philippines <0.05 mg/kg (2). An STMR was estimated from the residues in the pulp of unbagged bananas: 0.03, 0.03, 0.04, 0.11, 0.13 and 0.17 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg, the same as the current CXL, and an STMR of 0.075 mg/kg.

Tomatoes. Ten trials were carried out in The Netherlands according to GAP with 3 x 0.03 kg ai/hl in a greenhouse. At the GAP PHI of 3 days the residues in normal sized tomatoes ranged from 0.39 to 0.98 mg/kg. In cherry tomatoes, the residues were twice as high: 2.1 and 2.4 mg/kg. All the residues in normal and cherry tomatoes in rank order were 0.39, 0.41, 0.48, 0.54, 0.56, 0.96, 0.96, 0.98, 2.1 and 2.4 mg/kg.

The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.76 mg/kg for tomatoes.

Cucumbers. Greenhouse trials were carried out in southern France (2) and The Netherlands (8).

The French trials (3 x 0.02 kg ai/hl, PHI 17 days) were not according to GAP.

The residues in the 8 trials carried out in The Netherlands according to GAP (3 x 0.03 kg ai/hl) in rank order were 0.1, 0.11, 0.16, 0.17, 0.19, 0.21, 0.22 and 0.22 mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg (the same as the existing CXL) and an STMR of 0.18 mg/kg for cucumbers.

Common beans, bean forage, peanuts, peanut forage. As no data on GAP or residue trials were provided, the Meeting agreed to recommend the withdrawal of the CXLs of 0.5 mg/kg for common bean, 10 mg/kg for bean forage, 0.1* mg/kg for peanut and 20 mg/kg for peanut forage (green).

Seed treatments

Barley. The highest application rates are in Sweden (0.07 kg ai/100 kg seed) and The Netherlands (0.056 kg ai/100 kg seed). Eight supervised trials were conducted in Germany, 6 with 0.07-0.075 kg ai/100 kg seed according to Swedish GAP and 2 with 0.057 kg ai/100 kg seed according to GAP in The Netherlands. The residues were below the LOD of 0.05 mg/kg in grain harvested 100 to 144 days after treatment in all the samples.

Oats. The highest application rates are in Sweden (the same as barley) and Austria (0.038-0.075 kg ai/100 kg seed). In Germany, The Netherlands and the UK the rate is 0.056 kg ai/100 kg seed. Seven supervised trials were conducted in Germany, 3 at 0.075 kg ai/100 kg seed according to Swedish GAP and 4 at 0.055-0.057 kg ai/100 kg seed according to GAP in Germany, The Netherlands and the UK. The residues were below the LOD of 0.05 mg/kg in all samples harvested 113 to 147 days after treatment.

Rye. The highest application rates are in Austria (0.038-0.075 kg ai/100 kg seed), Germany, The Netherlands, Sweden and the UK (all 0.056 kg ai/100 kg seed). In nine trials in Germany, 8 were with 0.056 kg ai/100 kg seed and 1 with 0.07 kg ai/100 kg seed. The residues were below the LOD of 0.05 mg/kg in all grain samples harvested 289 to 322 days after treatment.

Wheat. The highest application rates are in Germany (0.075 kg ai/100 kg seed), Poland (0.07 kg ai/100 kg), Sweden (0.056-0.07 kg ai/100 kg), The Netherlands (0.056 kg ai/100 kg) and the UK (0.038-0.056 kg ai/100 kg). In Germany 11 supervised trials were carried out on spring wheat and 2 on winter wheat at 0.07-0.076 kg ai/100 kg. The residues were below the LOD of 0.05 mg/kg in all the grain samples.

Triticale. Uses are registered in Denmark, Poland and the UK and are identical with those for wheat and/or rye in those countries. The Meeting agreed to extrapolate the results from wheat and rye to triticale.

The Meeting estimated a maximum residue level of 0.05* mg/kg for bitertanol in barley, oats, rye, triticale and wheat as being a practical limit of determination, and recommended the withdrawal of the existing CXLs for oats, rye and wheat (0.1* mg/kg). As the residues were below the LOD in all samples, and this was consistent with the results of a metabolism study with [^{14}C]bitertanol where no parent compound was detected in the grain at harvest, an STMR of 0 mg/kg was estimated.

Straw and fodder of cereal grains. Supervised trials according to GAP in several European (0.056-0.075 kg ai/100 kg seed) were carried out on barley (8), oats (7), rye (9) and wheat (13). The residues in all straw and forage samples were below the LOD of 0.05 mg/kg.

The Meeting agreed to recommend the withdrawal of the current CXLs for straw and fodder (dry) of oats, rye and wheat of 0.1* mg/kg. A maximum residue level of 0.05* mg/kg was estimated for the straw and fodder (dry) of barley, oats, rye, triticale and wheat as a practical limit of determination. As no detectable residue is to be expected in cereal straw after seed treatment, an STMR of 0 was estimated.

Oat and rye forage. Cereals such as oats and rye are grown to a limited extent as forage crops. The immature crop is fed to livestock animals as succulent forage or as silage.

Seven supervised trials on oats and 9 on rye with seed treatments of 0.055-0.075kg ai/100 kg seed were reported. Green oats and rye were harvested at 63-101 and 218-254 days after application respectively. The residues were not detected in any of the green plants.

The Meeting recommended replacement of the current CXLs for oat and rye forage (green) of 0.1* mg/kg by 0.05* mg/kg (dry weight basis) as a practical limit of determination. According to the results of the metabolism study, the possibility of residues of bitertanol in cereal forage after seed treatment cannot be excluded, and an STMR of 0.05 mg/kg was estimated.

Animal feeding studies

Groups of 3 cows were dosed by capsule for 28 days with bitertanol at levels corresponding to 25, 75 and 250 ppm in the feed or 0.63, 1.88 and 6.25 mg/kg bw per day. Milk samples were collected from all cows on days 0, 7, 14, 21 and 28. At the end of the test period, the animals were slaughtered and their tissues and milk analysed for total extractable bitertanol and metabolite residues. The results are summarized in the following table.

Dose mg/kg bw/day	Total bitertanol residues, mg/kg									
	Milk		Liver		Kidney		Muscle		Fat	
	high	mean	high	mean	high	mean	high	mean	high	mean
0.63	0.01	<0.01	0.78	0.63	0.05	0.037	0.06	0.03	0.06	0.027
1.88	0.07	0.04	1.9	1.4	0.36	0.32	0.09	0.08	0.18	0.17
6.25	0.26	0.24	3.7	2.8	1.1	0.77	0.44	0.32	1.3	0.85

In a metabolism study on a dairy cow dosed for 5 days with 0.2 mg/kg bw/day the milk contained only 0.008 mg/kg bitertanol equivalents (0.2% of the applied ^{14}C) but the residues had not reached a plateau. In the tissues the total ^{14}C residues were liver 0.82, kidney 0.11, muscle 0.01 and fat 0.03 mg/kg bitertanol equivalents.

As the residue of bitertanol in the milk reached a plateau slowly (3-4 weeks after treatment at the earliest), the STMRs of the feed items should be used to estimate the dietary burden. The highest exposure to bitertanol residues may arise from the consumption of wet apple pomace with an STMR level of 0.648 mg/kg. With the theoretical assumption that the daily maximum feed consumption of beef cattle (body weight 550 kg) would be 20 kg on a dry matter basis, including 40% of wet pomace (containing 40% dry matter), the intake may be calculated as follows.

0.648 mg/kg wet weight is equivalent to 1.62 mg/kg on a dry matter basis.
As apple pomace forms 40% of the diet it will contribute 1.62 x 0.4 = 0.648 ppm in the total feed on a dry matter basis.
On this basis beef cattle may be exposed to 0.0236 mg bitertanol/kg bw/day.

The lowest dose rate in the feeding study represents approximately 27 times the estimated dietary burden (0.63/0.0236). The Meeting noted the high ratio and concluded that an extrapolation downwards to the real intake would result in residues below the 0.05 mg/kg reported as a practical limit of determination in the official method of analysis of The Netherlands.

The Meeting estimated 0.05* mg/kg as a maximum residue level for milk, edible offal and meat (fat) and 0.05 mg/kg as an STMR for milk, edible offal and meat. As the metabolism is similar in rats and cows, these levels are estimated for cattle, goats, sheep and pigs.

A metabolism study in hens showed that approximately 98% of the dose was recovered in the excreta. Eggs contained <0.2% of the total dose.

Laying hens (10 birds/group) were fed daily rations containing bitertanol at total residue levels of 1, 3 and 100 ppm for 28 days. Additional hens were fed the 100 ppm diet for 28 days and then maintained on untreated rations for an additional 14 days (five birds) or 28 days (three birds) before slaughter to determine the rate of decline of residues in the tissues and eggs. The tissues and eggs were analysed for total extractable bitertanol and metabolite residues.

Tissues from the 3 ppm and 100 ppm treatment groups were pooled in each group and analysed. Eggs from those groups were analysed at 7, 14, 21 and 28 days. The residues found in the 100 ppm group were liver 1.03 mg/kg, gizzard 0.23 mg/kg, heart 0.10 mg/kg, muscle 0.07 mg/kg and fat 0.07 mg/kg. Liver, gizzard and muscle samples from the 3 ppm group contained quantifiable residues, the liver having the highest level (0.21 mg/kg), followed by gizzard (0.07 mg/kg) and muscle (0.01 mg/kg). The residues in the livers at the lowest feeding level (1 ppm) were below 0.01 mg/kg, and other tissues were not

analysed as the residues from the higher dose rates were so low. The residues in eggs were only quantifiable in the 100 ppm feeding group; day 28 eggs from that group contained 0.11 mg/kg bitertanol. All tissue and egg residue levels in the residue decline group were below 0.01 mg/kg 28 days after the birds had been returned to untreated feed except in the liver, which contained 0.04 mg/kg).

The exposure to bitertanol residues would arise from cereal grains, with a maximum residue level of 0.05* mg/kg (STMR 0 mg/kg).

With the theoretical assumption that the daily maximum feed consumption of a chicken (bw 1.9 kg) is 0.12 kg dry matter consisting of 100% cereal grains (e.g. wheat or oats with 89% dry matter) the intake may be calculated as follows.

A maximum residue of 0.05 mg/kg wet weight is equivalent to 0.056 mg/kg on a dry weight basis.

As cereal grain forms 100% of the diet, the bitertanol residue in the total feed (dry matter basis) is equivalent to 0.056 ppm, and hence to an intake of 0.0035 mg/kg bw/day.

In view of the results of the metabolism and feeding studies, no residues are to be expected in edible tissues or eggs. The Meeting estimated an STMR of 0 and a maximum residue level of 0.01* mg/kg for eggs, poultry meat, and edible offal of poultry as a practical limit of determination.

Processing

Studies have been carried out to determine the effect of processing on residues of bitertanol in apples, cherries, peaches, plums and tomatoes.

Apples containing 0.08, 0.23, 0.55 and 1 mg/kg bitertanol were processed to juice and sauce, which did not contain residues above the LOD of 0.02 mg/kg.

In 2 further trials, the residues in raw apples were 0.49 and 8.2 mg/kg, in juice 0.09 and 0.84 mg/kg and in wet pomace 1.37 and 21 mg/kg. The wet pomace in the second trial (8.2 mg/kg in unprocessed apples) was processed to dry pomace, which contained a residue of 61 mg/kg (processing factor 7.4).

The Meeting agreed to calculate the STMR levels on the basis of the trials which included the determination of bitertanol in the pomace, which is a potential feeding-stuff. From the STMR of 0.24 mg/kg for apples and mean processing factors of 0.14 for juice and 2.7 for wet pomace as well as the factor of 7.4 for dry pomace, the Meeting estimated STMRs of 0.0336 mg/kg for apple juice and sauce, 0.648 for wet apple pomace and 1.78 mg/kg for dry apple pomace.

The processing data on stone fruit indicate that residues of bitertanol do not concentrate in any processed commodity which may be used as food. Three trials were carried out on cherries and 2 each on peaches and plums. The peach trials could not be evaluated as the residues in washed and unwashed fruit were inconsistent and it was not clear which fruit was further processed.

Cherries were processed into juice, preserve and jam, and plums into sauce and jam. The procedures for jam production were nearly identical for cherries and plums. The processing factors for cherry juice were 0.028, 0.115 and 0.375 (mean 0.17), for cherry jam 0.36 and 0.54 (mean 0.45), for cherry preserve 0.5, 0.58 and 0.68 (mean 0.59), and for plum jam 0.57 and 0.64 (mean 0.605).

On the basis of the mean processing factors and the STMRs of 0.365 mg/kg for cherries and 0.34 mg/kg for plums, the Meeting estimated the following STMRs. Cherries: 0.062 mg/kg juice, 0.16 mg/kg jam, 0.22 mg/kg preserve. Plum jam 0.21 mg/kg.

One processing study on tomatoes was reported. The residues of bitertanol were lower in juice and preserves (processing factors 0.135 and 0.365), but higher in paste (processing factor 2.1). The Meeting estimated STMRs of 0.1, 0.28 and 1.6 mg/kg for tomato juice, preserve and paste respectively, based on the STMR for tomato of 0.76 mg/kg.

RECOMMENDATIONS

The Meeting estimated the maximum residue and STMR levels shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue

For compliance with MRLs for plant and animal commodities: bitertanol.

For dietary intake for plant commodities: bitertanol.

For dietary intake for animal commodities: sum of bitertanol, *p*-hydroxybitertanol and the acid-hydrolysable conjugates of *p*-hydroxybitertanol.

The compound is fat-soluble.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
JF 0226	Apple juice			0.034
AB 0226	Apple pomace, dry			1.78
	Apple pomace, wet			0.648
	Apple sauce			0.035
FS 0240	Apricot	W	1	
FI 0327	Banana	0.5	0.5	0.075
GC 0640	Barley	0.05*	-	0
AS 0640	Barley straw and fodder, d``ry	0.05*	-	0
AL1030	Bean forage (green)	W	10	
FS 0013	Cherries	1	2	0.365
	Cherry jam			0.16
	Cherry juice			0.062
	Cherry preserve			0.22
VP 0526	Common bean (pods and/or immature seeds)	W	0.5	
VC 0424	Cucumber	0.5	0.5	0.18
MO 0105	Edible offal (Mammalian)	0.05*		0.05
PE 0112	Eggs	0.01*		0
MM 0095	Meat (from mammals other than marine mammals)	0.05* (fat)		0.05
ML 0106	Milks	0.05*		0.05
FS 0245	Nectarine	1	1	0.20
AF 0647	Oat forage (green)	0.05* (dry wt.)	0.1*	0.05
AS 0647	Oat straw and fodder, dry	0.05*	0.1*	0
GC 0647	Oats	0.05*	0.1*	0
FS 0247	Peach	1	1	0.20
SO 0697	Peanut	W	0.1*	
AL 1270	Peanut forage (green)	W	20	
FS 0014	Plums (including Prunes)	2	2	0.34
	Plum jam			0.21
FP 0009	Pome fruits	2	2	0.24
PM 0110	Poultry meat	0.01*		0
PO 0111	Poultry, Edible offal of	0.01*		0
GC 0650	Rye	0.05*	0.1*	0
AF 0650	Rye forage (green)	0.05* (dry wt.)	0.1*	0.05
AS 0650	Rye straw and fodder, dry	0.05*	0.1*	0

Commodity		MRL, mg/kg		STMR,
CCN	Name	New	Previous	mg/kg
VO 0448	Tomato	3	-	0.76
JF 0448	Tomato juice			0.1
	Tomato paste			1.6
	Tomato preserve			0.28
GC 0653	Triticale	0.05*	-	0
	Triticale straw and fodder, dry	0.05*	-	0
GC 0654	Wheat	0.05*	0.1*	0
AS 0654	Wheat straw and fodder, dry	0.05*	0.1*	0

W: withdrawal recommended

DIETARY RISK ASSESMENT

Chronic intake

International Estimated Daily Intakes (IEDIs) of bitertanol were estimated from the STMRs of 23 commodities.

International Estimated Daily Intakes for the five GEMS/Food regional diets, based on estimated STMRs, were in the range of 2% to 10% of the ADI. The Meeting concluded that the intake of residues of bitertanol resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The 1998 JMPR concluded that it was unnecessary to establish an acute RfD because bitertanol has been classified by WHO as unlikely to present an acute hazard in normal use and has not shown any specific adverse effects (teratogenicity, neurotoxicity) after single doses 100 times the lowest relevant NOAEL in long- and short-term studies that were used to establish the ADI. The Meeting therefore concluded that the short-term dietary intake of bitertanol residues is unlikely to present a risk to consumers.

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82614 Obrist, J.J. and Puhl, R.J. 1986
84062 Obrist, J.J., Puhl, R.J. and Thornton, J.S. 1983
84222 Mobay Chemical Corporation 1983b
84571 Mobay Chemical Corporation, 1984a
84264 Mobay Chemical Corporation, 1984b
85832 Puhl, R.J. and Hurley, J.B. 1983
86315 Leimkuehler, W.M., Cain, K.S., Whitefield, S.L. and Clay, V.E. 1983
86466 Sandie, F.E. and Thornton, J.S., 1984
87036 Mobay Chemical Corporation 1985
88161/V16-A S. African Bureau of Standards, 1982b
88161/V16-B S. African Bureau of Standards, 1982b
88352/W26-A S. African Bureau of Standards, 1983c
88352/W26-B S. African Bureau of Standards, 1983c
88352/W26-C S. African Bureau of Standards, 1983c
88355/W29-A S. African Bureau of Standards, 1983d
88355/W29-B S. African Bureau of Standards, 1983d
88355/W29-C S. African Bureau of Standards, 1983d
88419/W212-A S. African Bureau of Standards, 1983a
88419/W212-B S. African Bureau of Standards, 1983a
88421/W214-A S. African Bureau of Standards, 1983b
88421/W214-B S. African Bureau of Standards, 1983b
88736/B140-A S. African Bureau of Standards, 1985
88736/B140-B S. African Bureau of Standards, 1985
88736/B140-C S. African Bureau of Standards, 1985
88736/B140-D S. African Bureau of Standards, 1985
FM 320 Wilmes, R. 1980
FM 336 Wilmes, R. 1981
FM 759 Burhenne, J. 1996
M 7596 Thielert, W. and Kuck, K.H. 1992
M 9557 Fent, G. 1997
MR 68273 Nichols, S.S. and Thornton, J.S. 1979
MR 84126 Leimkuehler, W.M. 1983
MR 86103 Sietsema, W.K. 1983
MR 86131 Mobay Chemical Corporation 1984d
MR 86312 Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1984b
MR 86316 Mobay Chemical Corporation 1984c
MR 86317 Leimkuehler, W.M., Cain, K.S., Whitfield, S.L. and Clay, V.E. 1984a
MR 935/97 Allmendinger, H.1998
NR 1134 Takase, I. and Yoshimoto, Y. 1980
PF 3076 Klein, O. 1988a.
PF 3096 Klein, O. 1988b.
PF 3366 Fritz, R. 1990
PF 3501Klein, O. 1991
PF 3544 Hellpointner, E. 1991
PC 618 Krohn, J. 1989
PC 622 Krohn, J. 1992
PC 620 Herrmann, U. 1981a
PC 621Herrmann, U. 1981b
PC 627 Klusacek, H. 1986
PC 628 Mobay Chemical Corporation 1984e
RA 75/86 Brennecke, R. 1986
RA 2112/96 Nüßlein, F. 1998b
RA 1272/82 Brennecke, R. 1982a
RA 981/83 Brennecke, R. 1983a
RA 2104/96 Nüßlein, F. 1998e
RA 2010/91 Krebber, 1992
RA 2010/93 Nüßlein, F. 1996
RA 2011/93 Bachmann, 1995
RA 2059/96 Nüßlein, F. 1998d
RA 2083/94 Nüßlein, F. and Walz-Tylla, B. 1996
RA 2096/96 Nüßlein, F. 1998c
RA 2111/96 Nüßlein, F. 1997
RA 2113/96 Nüßlein, F. 1998a
RA 212/93 Köhler, J. 1993
RA 2166/97 Heinemann O. and Allmendinger, H. 1998

BUPROFEZIN (173)

EXPLANATION

Buprofezin was first evaluated by the 1991 JMPR which established an ADI of 0-0.01 mg/kg bw and recommended temporary MRLs for oranges, cucumber and tomato pending the delivery of required information by 1995.

The 1995 JMPR reviewed the submitted information and concluded that the data were adequate to recommend MRLs for cucumbers and tomatoes but inadequate for citrus fruits, and recommended that the existing temporary MRL for oranges be withdrawn. It was further concluded that if citrus MRLs were contemplated in a future submission a citrus processing study, including analyses for the main residues identified in the metabolism study (e.g. buprofezin, metabolite A and the thiobiuret derivative unless it had been shown not to be formed during citrus metabolism) would be required, and experimental evidence that the thiobiuret does not occur during citrus metabolism would be desirable.

The 1995 JMPR also listed the following items as desirable.

1. Analysis of reserve cow liver and kidney samples from the ruminant metabolism studies for the presence of dihydroxybuprofezin, hydroxymethoxybuprofezin and the thiobiuret metabolite.

2. A conventional animal processing study to determine residues of buprofezin, *p*-hydroxybuprofezin and (in milk) *p*-acetamidophenol.

The 1998 Session of the CCPR noted that buprofezin would be reviewed by the 1999 JMPR and that data from additional residue trials on oranges would be submitted (ALINORM 99/24, para 76).

The Meeting received information on follow-up studies on metabolism in a lactating dairy cow and in lemons, GAP for fruits, vegetables and almonds, residue trials on oranges, a feeding study on dairy cows and a processing study on oranges. Further information was provided by the governments of Germany, The Netherlands, Poland and the UK.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Huang and Smith (1997) re-examined residues in tissues from a previously reported study of metabolism in a lactating cow (Huang and Smith, 1995) in an effort to identify more of the residue in the liver, kidneys and milk. Despite extensive additional clean-up and attempts at identification no new metabolites were identified. The measured levels of metabolites differed slightly from the original (Table 2, page 28 of the 1995 Residue Evaluations). The large amount of unextractable and polar residue was taken as evidence of extensive conjugation.

Despite the extensive efforts no more than about 20-30% of the residue in the liver, kidneys and milk could be identified (Table 1) but the levels of individual unknown compounds were low, the highest being 0.07 mg/kg buprofezin equivalents in liver. An additional 13 compounds synthesised as possible metabolites were available as standards for identification, including 1-*tert*-butyl-3-isopropyl-5-phenyl-2-thiobiuret (BF-25, the ‘thiobiuret’ hydrolysis product) and 2-*tert*-butylimino-5-(4-

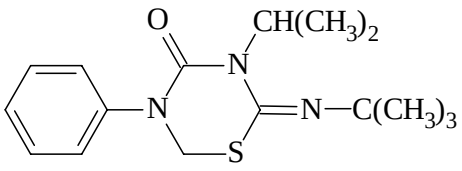
hydroxy-3-methoxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one (BF-27, the 'hydroxymethoxy-buprofezin' metabolite identified in rats). Neither was detected in the milk or tissues of the cow.

Table 1. Levels of [^{14}C]buprofezin and its metabolites in tissues and milk from a lactating cow (Huang and Smith, 1997).

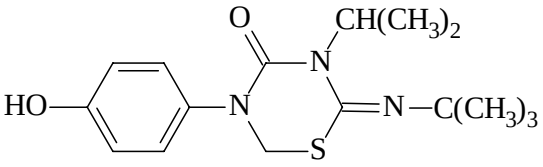
Compound	Liver		Kidneys		Milk	
	^{14}C as buprofezin, mg/kg	^{14}C as % of total in sample	^{14}C as buprofezin, mg/kg	^{14}C as % of total in sample	^{14}C as buprofezin, mg/kg	^{14}C as % of total in sample
Buprofezin		nd		nd	0.0007	2.2
BF2	0.13	10.9	0.07	18	0.0007	2.4
BF12	0.04	3.5	0.02	3.9	0.0011	3.6
BF13	0.03	2.5	0.01	3.1		nd
BF23	0.03	2.2	0.03	7.7	0.0041	13.7
Largest unknown	0.071	5.9	0.019	4.5	0.0009	2.9
Total identified	0.23	19.1	0.13	32.7	0.0066	21.9
TOTAL ^{14}C	1.21		0.41		0.03	

nd: not detected

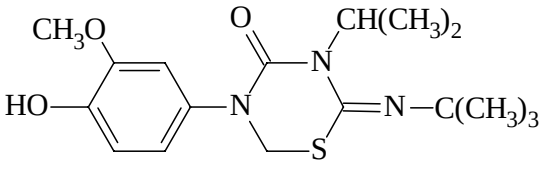
The structures of buprofezin, the bovine metabolites, and the comparison compounds BF-25 and BF-27 are shown below.



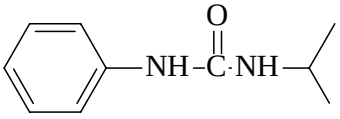
buprofezin



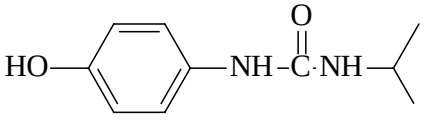
p-hydroxybuprofezin (BF-2)



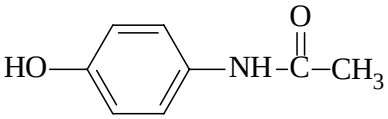
2-*tert*-butylimino-5-(4-hydroxy-3-methoxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one (BF-27)



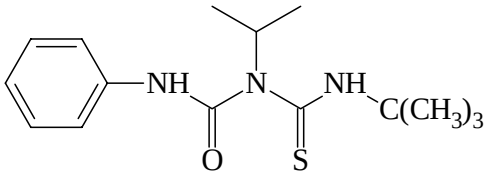
isopropylphenylurea (BF-12)



hydroxy-IPU (BF-13)



p-hydroxyphenylacetamide (BF-23)



1-*tert*-butyl-3-isopropyl-5-phenyl-2-thiobiuret (BF-25)

Plant metabolism

Smith (1997) re-examined the metabolites in extracts from the study of metabolism in lemons (Rieser and Smith, 1995) reviewed by the 1995 JMPR. The purpose was to determine the identity of the residue that produced 2-amino-2-methylpropyl 2-isopropyl-4-phenylallophanate (BF-26) on acid hydrolysis and to examine the extracts for the thiobiuret BF-25.

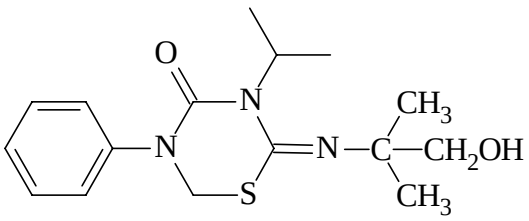
Extracts containing conjugates were cleaned up by preparative HPLC and examined by LC-MS. The molecular weight of the major conjugate was 484, which is consistent with 2-(2-hydroxy-1,1-dimethylethylimino)-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one (BF-4) linked to a hexose. After acetylation with acetic anhydride in pyridine the molecular weight of the conjugate was 652, demonstrating the incorporation of 4 acetyl groups, again consistent with a hexose conjugate of BF-4.

Hydrolysis of fractions containing conjugates was attempted with mild base and ∃-glucosidase but this released only 16-17% of the ^{14}C from which small amounts of BF-26 and BF-12 were identified. Enzymatic hydrolysis with ∀-glucosidase again released only a little of the ^{14}C from the conjugate. Metabolite BF-26 was identified in this hydrolysate. The original study had shown that strong acid hydrolysis of the main residue produced BF-26, BF-9 and BF-12, and mild acid hydrolysis of synthetic BF-4 produced BF-26 and BF-9.

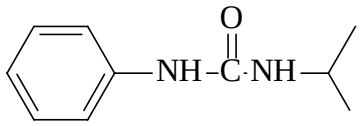
The evidence suggests that the main metabolite of buprofezin in lemons is a non-glucose hexose conjugate of BF-4. The BF-4 cannot be liberated from the conjugate without further degradation to BF-26, BF-9 and BF-12.

Unhydrolysed extracts from the lemons were examined for BF-25 but none was detected.

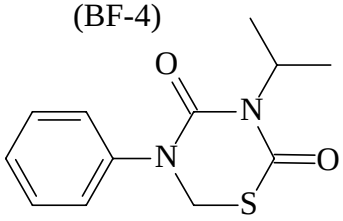
The structures of BF-4, the hydrolysis products, and BF-25 are shown below.



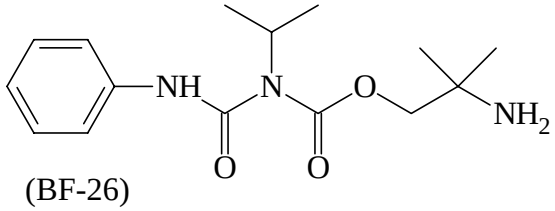
(BF-4)



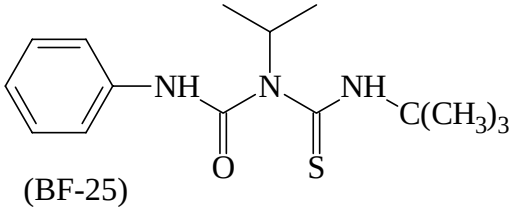
isopropylphenylurea (BF-12)



(BF-9)



(BF-26)



(BF-25)

METHODS OF RESIDUE ANALYSIS

Analytical methods

The Meeting received information on the GLC methods used to determine buprofezin and some metabolites in oranges and orange commodities in supervised trials, processing studies and animal feeding studies, and in kidneys, liver, fat, muscle and milk.

Barnard (1998) used analytical procedure NHH/089-01R to determine buprofezin, BF-9 and BF-12 in orange homogenate during freezer storage stability trials. The residues were extracted with acetone, the extract was acidified with hydrochloric acid and the acetone evaporated to leave an aqueous phase. This was washed with hexane, then neutralised with sodium hydroxide and pH 7 buffer, and the residues were extracted into dichloromethane. The dichloromethane was evaporated and the residue taken up in hexane and cleaned up on an aminopropyl solid-phase extraction cartridge to yield a fraction which contained the buprofezin for determination by GLC with an NPD. A separate portion of the original acetone extract was analysed for BF-9 and BF-12. The extract was diluted with pH 7 buffer and evaporated to leave an aqueous phase from which the residues were extracted with dichloromethane. The dichloromethane was evaporated and the analysis completed as above. Procedural recoveries at a fortification level of 0.1 mg/kg of 4 replicates of each analyte were buprofezin mean 80.5%, range 69-90%, BF-9 mean 92.3%, range 88-96%, and BF-12 mean 88.5%, range 78-97%.

Wilson (1997) used the same procedure for oranges, with an LOD for the three analytes of 0.01 mg/kg. Procedural recoveries at fortification levels of 0.1-0.5 mg/kg for each analyte (12 replicates) were buprofezin mean 85%, range 70-101%, BF-9 mean 87%, range 70-98%, and BF-12 mean 96%, range 75-109%.

Tymoschenko and Williams (1997) determined buprofezin residues in cattle tissues and milk. They extracted buprofezin and BF-12 from beef tissues with acetonitrile. This was diluted with hydrochloric acid and the residues partitioned into dichloromethane. The extract was evaporated and the residue dissolved in toluene for clean-up on an aminopropyl solid-phase extraction column. The residues in the eluate were determined by GLC with an MSD. The LODs for both buprofezin and BF-12 were 0.05 mg/kg. Recoveries from beef liver, kidneys, muscle and fat fortified at 0.05-0.20 mg/kg were buprofezin mean 96%, range 83-132%, and BF-12 mean 98%, range 83-135% (9 replicates). BF-2 was extracted with acetonitrile, the extract was washed with hexane, and the acetonitrile evaporated to dryness. The residue was taken up in pH 7 buffer and extracted with ethyl acetate. The ethyl acetate solution was evaporated to dryness, the residue was taken up in toluene, and the analysis completed as for buprofezin and BF-12. The LOD for BF-2 was 0.05 mg/kg. Recoveries from beef liver, kidneys, muscle and fat fortified at 0.05-0.20 mg/kg were mean 106%, range 82-118% (10 replicates).

Buprofezin and BF-12 were extracted from milk by mixture with acetonitrile, filtration, concentration, dilution with hydrochloric acid and partitioning into dichloromethane. The solvent was evaporated and the residue dissolved in toluene for clean-up and analysis as before. The LODs for buprofezin and BF-12 in milk were 0.01 mg/kg. Recoveries from milk fortified at 0.01 and 0.05 mg/kg were buprofezin mean 90%, range 69-112%, and BF-12 mean 91%, range 81-119% (16 replicates). To determine BF-23 in milk the mixture with acetonitrile was filtered, concentrated, diluted with sodium chloride, washed with hexane and partitioned into ethyl acetate. The ethyl acetate was evaporated, and the residue dissolved in toluene and cleaned up on a C-18 extraction column. The residue in the eluate was determined by GLC as before. The LOD for BF-23 was 0.01 mg/kg. Recoveries from milk fortified with BF-23 at 0.01 and 0.05 mg/kg were mean 98%, range 94-110% (4 replicates).

Neal (1997) described the method used for the determination of buprofezin, BF-9 and BF-12 in oranges, juice, oil and dry pulp. Oranges were extracted with acetone and the acetone evaporated to

leave an aqueous mixture which was acidified with hydrochloric acid. Hexane extracted BF-9 from the aqueous layer and the extract was cleaned up by Florisil column chromatography. Buprofezin and BF-12 were extracted from the remaining aqueous mixture with dichloromethane. The extract was combined with the cleaned-up BF-9 extract, the solvents evaporated and the residue dissolved in toluene before further clean-up on a solid-phase amino extraction column. The eluate was evaporated and the residue dissolved in toluene for analysis by GLC; the three analytes were readily separated. The initial extraction was modified for samples of juice, oil, and dry pulp. The LODs were 0.01 mg/kg for fruit and juice, 0.05 mg/kg for oil, and 0.1 mg/kg for dry pulp. Recoveries from whole oranges, oil, juice and dry pulp at spiking levels from 0.01 to 20 mg/kg were buprofezin mean 76%, range 41-103%, BF-9 mean 68%, range 46-88%, and BF-12 mean 84%, range 69-97% (9 replicates of each).

In the official method of The Netherlands (Ministry of Health, Welfare and Sport, 1996) buprofezin is determined in a multi-residue procedure by GLC with an ion-trap detector. The LOD is 0.05 mg/kg. The method produced good recoveries from various crop samples.

Stability of pesticide residues in stored analytical samples

Barnard (1998) determined the stability of buprofezin, BF-9 and BF-12 added to orange homogenate at 0.10 mg/kg in separate vials (10 g samples) and stored for 6 months at about -18°C (recorded daily maximum and minimum temperatures were mainly in the range -19°C to -11°C). Duplicate stored samples, a control and a procedural recovery sample were analysed by Method NHH/089-01R at each sampling.

The residues were apparently stable during the 6 months of storage (Table 2), but with the analytical error of the method at 0.1 mg/kg a 20-30% decrease would probably be needed to be noticeable.

Table 2. Percentage of buprofezin and metabolites remaining in fortified orange homogenate after storage at about -18°C for 6 months (Barnard, 1998). Results are not adjusted for recovery or control values.

Storage period	buprofezin		BF-9		BF-12	
	Stored sample, % of initial	Procedural recovery, %	Stored sample, % of initial	Procedural recovery, %	Stored sample, % of initial	Procedural recovery, %
0	86, 78	90	93, 84	92	93, 94	87
1 month	72, 71	69	92, 78	88	93, 89	78
3 months	75, 70	80	83, 99	96	97, 94	97
6 months	107, 77	91	74, 84	93	70, 75	92

Definition of the residue

The residue is defined as buprofezin, both for compliance with MRLs and for the estimation of dietary intake.

The log P_{ow} of 4.3 for buprofezin (JMPR residue evaluations, 1991) and the presence of buprofezin in body fat and milk fat but not in muscle or skimmed milk in a feeding study with dairy cows suggest solubility in fat. The Meeting agreed that buprofezin should be described as fat-soluble.

USE PATTERN

Details of the registered uses of buprofezin on citrus fruits in many countries were provided by the basic manufacturer, with copies of registered labels in some cases. Registered uses on vegetables in Europe, mainly glasshouse, were reported by national governments.

Table 3. Registered uses of buprofezin on citrus and other fruits, vegetables, and almonds.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Almond	Greece	25% WP	foliar		0.018		28
Aubergine	UK	250 g/l SC	foliar to run-off		0.0075	g 2	3
Citrus	Argentina	25% WP	foliar		0.013		14
Citrus	Brazil	25% WP	foliar		0.025-0.05		7
Citrus	China	25% WP	foliar		0.013-0.025	2	35
Citrus	Greece	25% WP	foliar		0.013-0.050		28
Citrus	Guatemala	25% WP	foliar	0.6			14
Citrus	Italy	40% SC	foliar		0.024-0.032		7
Citrus	Italy	25% WP	foliar		0.025-0.038		7
Citrus	Jordan	25% WP	foliar		0.013-0.038		14
Citrus	Lebanon	25% WP	foliar		0.013-0.038		14
Citrus	Portugal	25% WP	foliar		0.013		7
Citrus	South Africa	50% WP	foliar		0.015	2	45
Citrus	Spain	25% WP	foliar		0.01-0.013		7
Citrus	UAE	25% WP	foliar		0.013-0.038		14
Citrus	Uruguay	25% WP	foliar	0.25-1.0			14
Citrus except mandarin	Japan	25% WP	foliar		0.017-0.025	3	45
Courgette	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Courgette	Netherlands	250 g/l EC	foliar	0.030-0.060	0.0075	2	3
Cucumber	Belgium	250 g/l SC	foliar		0.0075	g	3
Cucumber	Germany	250 g/l SC	foliar	0.045-0.09	0.0075	g 3	3
Cucumber	Greece	25% WP	foliar		0.010-0.015	g	7
Cucumber	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Cucumber	Poland	25% WP	foliar	0.036-0.50	0.012-0.025	2-4	3
Cucumber	Switzerland	25 % WP	foliar		0.013	g	3
Cucumber	UK	250 g/l SC	foliar to run-off		0.0075	g 8	3
Egg plant	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Egg plant	Poland	25% WP	foliar	0.036-0.50	0.012-0.025	2-4	3

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Gherkin	Germany	250 g/l SC	foliar	0.045-0.09	0.0075	g 3	3
Gherkin	Netherlands	250 g/l EC	foliar	0.030-0.060	0.0075	2	3
Gherkin	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Grapes	See Vines						
Mandarin	Japan 🗎	25% WP	foliar		0.017-0.025	3	14
Melons	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Melons	Switzerland 🗎	25 % WP	foliar		0.013	g	3
Olive	Greece 🗎	25% WP	foliar		0.019-0.025		40
Peach	Greece 🗎	25% WP	foliar		0.025		14
Peppers	Switzerland 🗎	25 % WP	foliar		0.013	g	3
Peppers, sweet	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Peppers, sweet	Poland	25% WP	foliar	0.036-0.50	0.012-0.025	2-4	3
Peppers, sweet	UK 🗎	250 g/l SC	foliar to run-off		0.0075	g 2	3
Tomato	Belgium 🗎	250 g/l SC	foliar		0.0075	g	3
Tomato	Germany	250 g/l SC	foliar	0.045-0.09	0.0075	g 3	3
Tomato	Greece 🗎	25% WP	foliar		0.010-0.015	g	7
Tomato	Netherlands	250 g/l EC	foliar	0.037-0.11	0.0075	g 2	3
Tomato	Poland	25% WP	foliar	0.036-0.50	0.012-0.025	2-4	3
Tomato	Switzerland 🗎	25 % WP	foliar		0.013	g	3
Tomato	UK 🗎	250 g/l SC	foliar to run-off		0.0075	g 8	3
Vines	Switzerland 🗎	25 % WP	foliar	0.25			

g: glasshouse use
🗎: label (and English translation) provided.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on field trials on oranges in Italy and Spain and on a feeding study with lactating dairy cows.

Where residues were not detected they are recorded in the Tables as below the limit of determination (LOD), e.g. <0.01 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although trials included control plots, no control data are recorded in the tables except where residues in control samples exceeded the LOD. Residues are not corrected for recoveries.

Buprofezin sprays were applied to orange orchards in Italy and Spain with backpack lance sprayers that were calibrated before each application. Plot sizes were 340-450 m^2 or 3 rows each of 5 trees. Field samples consisted of 12-15 oranges (>2 kg) taken from the middle 3 trees of the central row. Samples were stored frozen until analysis for about 120-130 days.

Table 4. Buprofezin and metabolite residues in oranges resulting from supervised trials in Italy and Spain. Residues in field samples from replicate plots in one trial are shown separately. Whole oranges analysed. Double-underlined residues are from treatments according to GAP and were used to estimate a maximum residue level.

Country (location), year (variety)	Form	kg ai/ha	kg ai/hl	No.	PHI, days	Residue, mg/kg			Ref
						buprofezin	BF-9	BF-12	
Spain (Ayamonte), 1997 (Salustiano)	WP	0.26	0.013	1	7	0.06 0.04	<0.01 (2)	<0.01 (2)	NHH/089-01
Spain (Ayamonte), 1997 (Salustiano)	WP	0.52	0.026	1	7	0.13	<0.01	<0.01	NHH/089-01
Spain (Villaverde del Rio), 1997 (Navelino)	WP	0.26	0.013	1	7	0.07 0.06	<0.01 (2)	<0.01 (2)	NHH/089-02
Italy (Lentini), 1997 (Moro)	WP	0.51	0.025	1	7	0.26 0.26	<0.01 (2)	<0.01 (2)	NHH/089-03
Italy (Lentini), 1997 (Moro)	WP	1.0	0.051	1	7	0.43	<0.01	<0.01	NHH/089-03
Italy (Catania), 1997 (Tarocco)	WP	0.51	0.025	1	7	0.24 0.18	<0.01 (2)	<0.01 (2)	NHH/089-04

Groups of 3 lactating Holstein dairy cows (each animal weighing 370-699 kg) were dosed twice daily by gelatin capsule with 119, 357 or 1190 mg buprofezin per cow per day, equivalent to 5, 15 or 50 ppm in the feed, for 28 days (Tymoschenko and Williams, 1997). The animals consumed 17.4-28.2 kg feed/day (range of means), of which 85.6% was dry matter. Milk was collected regularly for analysis. On day 29 all the animals were slaughtered and liver, kidneys, perirenal fat and hindquarter muscle were analysed. Muscle and kidneys were dissected free from fat, and fat free from connective tissue, before analysis (Helsten, 1997).

The residues in milk are shown in Table 5. Buprofezin itself was detected only at the highest feeding level and in only 1 of the 3 animals, with the first detection on day 2. When day 28 milk was separated into skimmed milk and cream no residues were detected in the skimmed milk, but buprofezin was found in the cream from cows in the two higher dose groups.

BF-23 was detected in milk from control animals on days 24 and 28 as well as from cows in the 15 and 50 ppm groups. The residues were all 0.01 mg/kg, suggesting possible contamination. BF-23 is the analgesic acetaminophen or paracetamol, so contamination from other sources is possible. BF-12 was not detected in milk, skimmed milk or cream.

The residues in the tissues are shown in Table 6. BF-12 and BF-2 were not detected in any sample. Buprofezin was detected in the liver of one animal from the 50 ppm dose group at the LOD and in the fat of the 3 animals from the same group at 0.07, 0.11 and 0.12 mg/kg.

The intervals between sampling and analysis were 120 days for milk, 160 days for tissues, and 220 days for cream and skimmed milk. Information on the freezer storage stability of buprofezin

and its metabolites in animal commodities is needed to validate the study. Tymoschenko and Williams (1997) refer to such a study, but it was not available to the Meeting.

Table 5. Residues of buprofezin, BF-12 and BF-23 in milk collected during 28 days from cows dosed at 119, 357 or 1190 mg buprofezin per cow per day, equivalent to 5, 15 or 50 ppm in the diet (Tymoschenko and Williams, 1997). Residues are recorded for individual animals. Blank cells in the table denote no analyses.

Day	Residues, mg/kg								
	Buprofezin			BF-12			BF-23		
	5 ppm	15 ppm	50 ppm	5 ppm	15 ppm	50 ppm	5 ppm	15 ppm	50 ppm
1			<0.01 (3)			<0.01 (3)			
2			<0.01 (2) 0.02			<0.01 (3)			
4			<0.01 (2) 0.01			<0.01 (3)			
7			<0.01 (2) 0.01			<0.01 (3)			
10			<0.01 (2) 0.02			<0.01 (3)			
14			0.01 <0.01 0.02			<0.01 (3)			
17			<0.01 (2) 0.01			<0.01 (3)			
21			<0.01 (2) 0.02			<0.01 (3)			
24	<0.01 (3)	<0.01 (3)	<0.01 (2) 0.01	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3) c	0.01 (2) <0.01 c	0.01 <0.01 (2) c
28	<0.01 (3)	<0.01 (3)	<0.01 (2) 0.01	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3) c	<0.01 (3) c	0.01 <0.01 (2) c
Skimmed milk 28 days	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)			
Cream, 28 days	<0.01 (3)	0.01 (3)	0.03 (2) 0.05	<0.01 (3)	<0.01 (3)	<0.01 (3)			

c: residues of BF-23 at 0.01 mg/kg were reported in the milk from control animals in all groups on days 24 and 28

Table 6. Residues of buprofezin and BF-12 and BF-23 in tissues from the cows of Table 5 slaughtered on day 29 (Tymoschenko and Williams, 1997). Residues are recorded for individual animals.

Sample	Residues, mg/kg, of buprofezin and metabolites in tissues								
	Buprofezin			BF-12			BF-2		
	5 ppm	15 ppm	50 ppm	5 ppm	15 ppm	50 ppm	5 ppm	15 ppm	50 ppm
Liver	<0.05 (3)	<0.05 (3)	<0.05 (2) 0.05	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)
Kidneys	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)
Fat, perirenal	<0.05 (3)	<0.05 (3)	0.11 0.07 0.12	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)
Muscle	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)	<0.05 (3)

Table 7. Interpretation table for buprofezin residues in oranges from the trials in Table 4 and from the 1991 and 1995 evaluations. GAP and trial conditions are compared for treatments considered valid for maximum residue level and STMR estimations.

Crop	Country	Use pattern				Trial[1]	buprofezin
		kg ai/ha	kg ai/hl	No of appl.	PHI days		mg/kg
Citrus	Italy GAP		0.025-0.038		7		
Orange	Italy trial	1.0	0.051	1	7	NHH/089-03	0.43
Orange	Italy trial	0.51	0.025	1	7	NHH/089-03	0.26
Orange	Italy trial	0.51	0.025	1	7	NHH/089-04	0.24
Orange	Spain trial	1	0.025	1	7	JMPR 1995	0.06
Orange	Spain trial	1	0.025	1	7	JMPR 1995	0.03
Orange	Spain trial	1	0.025	1	7	JMPR 1995	0.03
Orange	Spain trial	0.52	0.026	1	7	NHH/089-01	0.13
Citrus	Spain GAP		0.010-0.013	1	7		
Orange	Spain trial	0.26	0.013	1	7	NHH/089-01	0.06
Orange	Spain trial	0.26	0.013	1	7	NHH/089-02	0.07
Citrus	South Africa GAP		0.015	2	45		
Orange	South Africa trial	2.25 g/tree	0.015	2	42	JMPR 1991	0.02

[1]JMPR 1995: Residue Evaluations, 1995, Buprofezin Table 8.
JMPR 1991: Residue Evaluations, 1991, Buprofezin Table 4.

Residues in animal commodities

When treated oranges are processed buprofezin residues find their way into orange pulp, which is used as animal feed. The Meeting estimated the dietary burden of residues for cattle using the diets in Appendix IX of the FAO Manual. The estimated dietary burden for beef and dairy cattle calculated from the maximum residue level in the feed item is equivalent to 0.45 ppm in the diet (Table 8) and is suitable for estimating maximum residue levels for the animal commodities. A similar calculation from the STMR for processed dry orange pulp (0.27 mg/kg) produces a dietary level of 0.059 ppm and is suitable for estimating STMR levels for animal commodities.

Table 8. Estimated dietary burden for beef and dairy cattle calculated from maximum residues in processed dry orange pulp and standard animal diets. DM is dry matter. MaxRes/DM is the maximum residue expressed on a dry-matter basis.

Commodity	MaxRes, mg/kg	DM, %	MaxRes/DM, mg/kg	% in diet		Residue in diet, ppm	
				Beef cattle	Dairy cattle	Beef cattle	Dairy cattle
Processed dry orange pulp	2.05	91	2.25	20%	20%	0.45	0.45

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Information was provided on the effects of processing oranges to juice, oil and dry pulp on the residue levels of buprofezin and its metabolites.

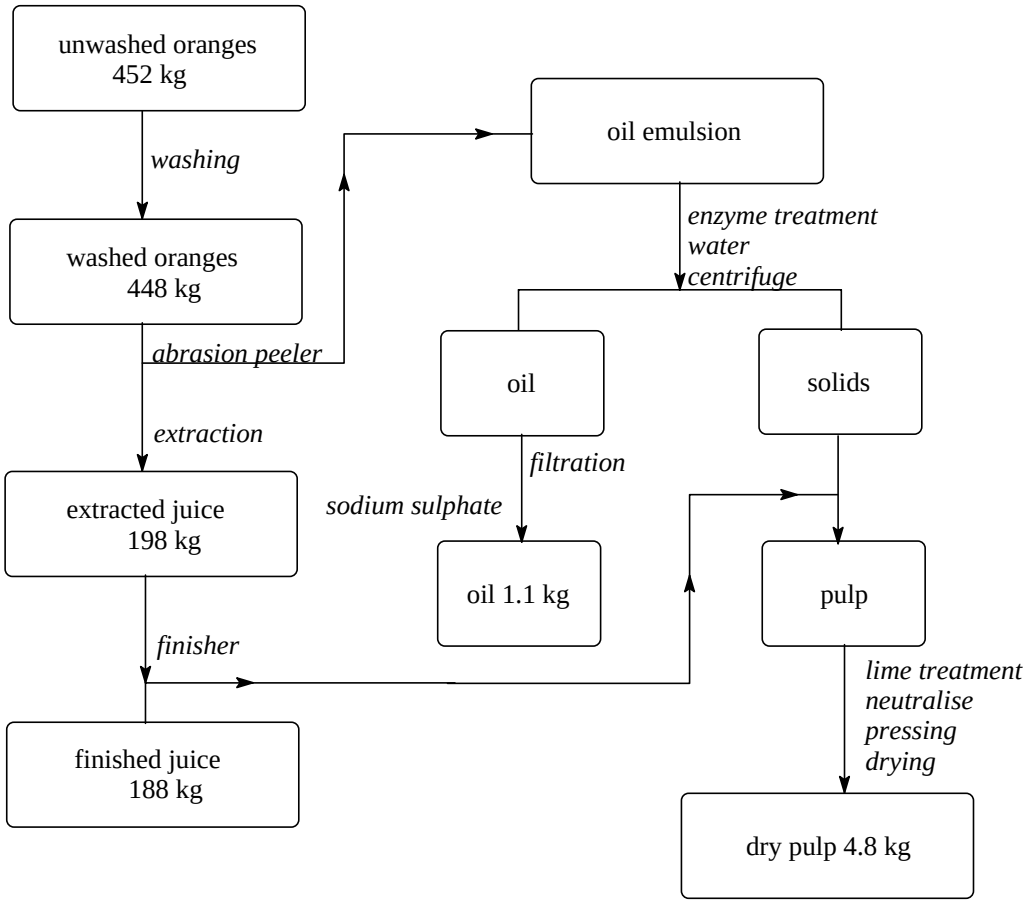
Neal (1997) treated Valencia orange trees twice (60 days interval) with buprofezin (Applaud® 70WP) at an exaggerated rate of 11 kg ai/ha (5 times the proposed maximum GAP rate) in California, USA, and harvested 460 kg oranges 66 days after the final treatment for processing.

The oranges were washed, abrasion peeled, and juiced, and the oil was extracted and the pulp dried in a simulated commercial process (Figure 1). The results are shown in Table 9, in which 'grower' refers to fruit sent directly from the orchard for analysis, and 'processor' to fruit sampled from the bulk delivered to the processor and representing the unwashed fruit entering the process. Freezer storage periods before analysis were fruit 149 days, oil 455 days, juice 147 days, and pulp 464 days. The freezer storage study on orange homogenate (Barnard, 1998) demonstrated adequate storage stability for 6 months but longer testing (possibly on related commodities) is needed to validate the processing study for oil and pulp.

Table 9. Residues of buprofezin and metabolites in oranges treated at an exaggerated rate of 11 kg ai/ha and in fractions produced during simulated commercial processing to oil, juice and dry pulp (Neal, 1997).

Commodity	Buprofezin, mg/kg, mean and (replicates)	BF-9, mg/kg, mean and (replicates)	BF-12, mg/kg, mean and (replicates)
Whole fruit (grower)	0.45 (0.59 0.43 0.35)	<0.01 (<0.01 (3))	0.01 (0.013 <0.01 0.016)
Whole fruit (processor)	0.27 (0.29 0.24 0.28)	<0.01 (<0.01 (3))	<0.01 (<0.01 (3))
Oil	11.6 (12.2 11.4 11.1)	0.17 (0.17 0.17 0.17)	<0.05 (<0.05(3))
Juice	0.049 (0.061 0.036 0.050)	0.01 (0.029 <0.01 <0.01)	0.01 (0.022 <0.01 <0.01)
Dry pulp	1.11 (0.98 1.11 1.23)	<0.1 (<0.1 (3))	0.14 (0.16 0.14 0.13)

Figure 1. Processing of oranges (Neal, 1997).



Residues in the edible portion of food commodities

Buprofezin residues in orange pulp, peel and whole fruit were recorded in a number of trials in the 1991 and 1995 residue evaluations, from which the ratio of the residues in the pulp to those in the whole fruit can be calculated. The mean ratio is 0.17 (Table 10).

Table 10. Ratio of residues in pulp to those in whole oranges from data recorded in the 1991 and 1995 JMPR residue evaluations.

Buprofezin residues in oranges, mg/kg		Ratio pulp/fruit	Trial	Ref.
whole fruit	pulp			
0.06	0.02	0.33	Spain 1994	JMPR 1995
1.12	0.0675	0.06	South Africa 1989	JMPR 1991
0.33	0.04	0.12	South Africa 1989	JMPR 1991
0.44	0.07	0.16	South Africa 1989	JMPR 1991
0.1975	0.0375	0.19	South Africa 1989	JMPR 1991
0.205	0.05	0.24	South Africa 1989	JMPR 1991
0.84	0.12	0.14	Portugal, 1987	JMPR 1991
0.76	0.12	0.16	Portugal, 1987	JMPR 1991
0.25	0.02	0.08	Portugal, 1987	JMPR 1991
		Mean 0.17		

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed that the following national MRLs had been established for buprofezin.

Country	MRL, mg/kg	Commodity
Netherlands[1]	0.2	Cucurbits (with edible peel)
Netherlands	0.2	Cucurbits (with inedible peel)
Netherlands	0*(0.05)	other food commodities
Poland	0.5	fruits and vegetables
Poland	0.1	other plant commodities

[1]Netherlands residue definition: buprofezin, parent compound, expressed as buprofezin

APPRAISAL

Buprofezin was first evaluated by the 1991 JMPR, which recommended a temporary MRL for oranges pending the delivery of required information by 1995.

The 1995 JMPR concluded that the available data were inadequate for citrus fruits and recommended that the existing temporary MRL for oranges be withdrawn. The 1995 Meeting also concluded that if citrus MRLs were contemplated in a future submission a citrus processing study, including analyses for the main metabolites, would be required, and experimental evidence that the thiobiuret metabolite does not occur during citrus metabolism would be desirable.

The 1995 JMPR also listed the following items as desirable.

1. Analysis of reserve cow liver and kidney samples from the ruminant metabolism studies for the presence of dihydroxybuprofezin, hydroxymethoxybuprofezin and the thiobiuret metabolite.

2. A conventional animal processing study to determine residues of buprofezin, *p*-hydroxybuprofezin and (in milk) *p*-acetamidophenol.

The Meeting received follow-up studies on metabolism in a lactating dairy cow and in citrus fruit, information on GAP and residue trials on citrus fruits, a feeding study on dairy cows and a processing study on citrus fruits. Further information was provided by Germany, The Netherlands, Poland and the UK.

Liver, kidney and milk samples from the previously reported study of metabolism in a lactating dairy cow were re-examined to identify more of the residue. Despite extensive additional clean-up and identification work no new metabolites were identified. The large amount of unextractable and polar residue was taken as evidence of extensive incorporation. No more than about 20-30% of the residue in the liver, kidneys and milk could be identified, but only in the liver did an unknown (at 0.07 mg/kg) exceed 0.05 mg/kg in a tissue, i.e. the levels of individual unknowns were low.

Additional standard compounds were available in the follow-up study, including 1-*tert*-butyl-3-isopropyl-5-phenyl-2-thiobiuret, the ‘thiobiuret’ hydrolysis product BF-25, and 2-*tert*-butylimino-5-(4-hydroxy-3-methoxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one, the ‘hydroxymethoxybuprofezin' metabolite BF-27 which was identified in rats. Neither was detected in the cow tissues or milk. The remaining possibility, the ‘dihydroxybuprofezin’ metabolite, was not included in the study but it is closely related to metabolite BF - 27, so desirable information point 1 (*analysis of reserve cow*

liver and kidney samples from the ruminant metabolism trials on the presence of the dihydroxybuprofezin, hydroxymethoxybuprofezin and the thiobiuret metabolites) is substantially satisfied.

Metabolites in extracts from the study of metabolism in lemons were re-examined to determine the identity of the residue that produced 2-amino-2-methylpropyl 2-isopropyl-4-phenylallophanate (BF-26) on acid hydrolysis and to check primary extracts for the presence of 1-*tert*-butyl-3-isopropyl-5-phenyl-2-thiobiuret (BF-25). Various enzyme hydrolyses were tried but released little of the bound ^{14}C. The evidence strongly suggests that the main metabolite is a non-glucose hexose conjugate of 2-(2-hydroxy-1,1-dimethylethylimino)-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one (BF-4). The BF-4 cannot be liberated from the conjugate without further degradation to BF-26, 3-isopropyl-5-phenyl-1,3,5-thiadazinane-2,4-dione (BF-9) and 1-isopropyl-3-phenylurea (BF-12). Unhydrolysed extracts from the lemons were examined by TLC for metabolite BF-25 (the 'thiobiuret' metabolite), but none was detected. This satisfies the request from the 1995 JMPR for *experimental evidence that the thiobiuret metabolite does not occur during citrus metabolism.*

Analytical methods for residues of buprofezin and some metabolites in oranges, orange commodities and kidney, liver, fat, muscle and milk were reported. The methods were used in the supervised trials, processing studies and animal feeding studies.

Samples were extracted and the extracts cleaned up by solvent partition and an aminopropyl solid-phase extraction cartridge, and analysed by GLC with an NPD. The exact procedure was tailored to the sample. LODs were in the range 0.01 to 0.1 mg/kg. Recoveries were usually in the 70-100% range, but individual recoveries dropped below 50% for residues in orange processing fractions.

Buprofezin, BF-9 and BF-12 added separately at 0.1 mg/kg to orange homogenate did not decrease perceptibly when stored for 6 months at approximately -18°C, but with the analytical error at levels of 0.1 mg/kg, a decrease of 20-30% would be necessary to be discernible.

The Meeting was informed that the results of a 1-year freezer storage stability study for residues in milk, fat and liver would be available in the year 2000.

The Meeting received information on registered uses of buprofezin on citrus fruits in 14 countries. It is usually applied as a foliar spray in the concentration range of 0.013-0.038 kg ai/hl, with typical intervals of 7-14 days specified before harvest, although South Africa has a 45 days PHI. Labels for uses on citrus were available from Italy, South Africa and Spain.

Supervised residue trials with buprofezin on oranges were reported from Spain and Italy, which included analyses for BF-9 and BF-12 as well as buprofezin.

In Spain buprofezin is registered for application to citrus trees with a spray concentration of 0.010-0.013 kg ai/hl and harvest 7 days later. Buprofezin residues were 0.06 and 0.07 mg/kg in oranges from 2 Spanish trials complying with GAP.

Buprofezin is registered for use on citrus trees in Italy at a spray concentration of 0.025-0.038 kg ai/hl. A ±30% tolerance on 0.038 kg ai/hl extends from 0.026 to 0.049 kg ai/hl so the trials, at 0.025 and 0.051 kg ai/hl, were at the margins of the allowable range of application rates. Trials on oranges in Italy and Spain complying with Italian GAP, including 3 trials reported in the 1995 Residue Evaluations, produced residues of 0.03, 0.03, 0.06, 0.13, 0.24, 0.26 and 0.43 mg/kg.

An orange trial in South Africa, reported in the 1995 Residue Evaluations, where buprofezin was used according to South African GAP (2 applications of 0.015 kg ai/hl, 45 days PHI) produced residues of 0.02 mg/kg.

In summary, buprofezin residues in 10 trials according to GAP in Italy, Spain and South Africa in rank order, median underlined, were 0.02, 0.03, 0.03, 0.06, 0.06, 0.07, 0.13, 0.24, 0.26 and 0.43 mg/kg. The STMR for whole oranges is 0.065 mg/kg.

The mean processing factor for orange pulp was 0.17, calculated from data in the 1991 and 1995 Residue Evaluations. The estimated STMR for buprofezin in the edible portion of oranges then becomes $0.065 \times 0.17 = 0.011$ mg/kg.

The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.011 mg/kg for buprofezin in oranges.

In a farm animal feeding study, dairy cows were dosed with buprofezin at the equivalent of 5, 15 and 50 ppm in the feed for 28 days. Buprofezin itself was detected in milk only at the highest feeding level and in only 1 of the 3 animals with the first detection occurring on day 2 and continuing only in this animal throughout the study. When day 28 milk was separated into skimmed milk and cream no residues were detected in the skimmed milk, but buprofezin residues were present in the cream from cows in the 15 and 50 ppm feeding groups. Metabolite BF-12 was not detected in milk, skimmed milk or cream. Metabolite BF-23 (acetaminophen or paracetamol) was detected in milk on days 24 and 28 both in samples from some treated groups and control samples, all at 0.01 mg/kg, suggesting contamination.

Buprofezin was detected at the LOD in the liver of one animal from the 50 ppm feeding group and at 0.07, 0.11 and 0.12 mg/kg in the perirenal fat of the 3 animals of the 50 ppm feeding group. The metabolites BF-12 and 2-*tert*-butylimino-5-(4-hydroxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one (*p*-hydroxy-buprofezin, BF-2) were not detected in any tissue. This provides the desirable information item 2 from the 1995 JMPR *a conventional animal transfer study in which residues of buprofezin, p-hydroxybuprofezin and (in milk) p-acetamidophenol are determined*.

The residue is defined as buprofezin, which is suitable both for compliance with MRLs and for the estimation of dietary intake. The buprofezin log P_{ow} of 4.3 (JMPR Residue Evaluations, 1991) and the presence of buprofezin in tissue fat and milk fat but not in muscle or skimmed milk in the dairy cow feeding study imply fat-solubility.

The Meeting agreed that buprofezin should be described as fat-soluble.

The Meeting received information on the fate of buprofezin and metabolites BF-9 and BF-12 during the processing of oranges to juice, oil and dry pulp. Oranges were harvested 66 days after treatment with buprofezin at an exaggerated rate (11 kg ai/ha). Fruit and juice were stored frozen for approximately 5 months before analysis, a period covered by the storage stability study on orange homogenate. Oil and dry pulp were stored for approximately 15 months before analysis without supporting evidence of stability for this period.

The calculated processing factors for buprofezin residues were oil 43, juice 0.18, and dry pulp 4.1. The residues of the metabolites were below or about the LOD (0.01 mg/kg) in the fruit so it is not possible to estimate processing factors, but BF-9 tended to be concentrated in the oil, while BF-12 was concentrated in the dry pulp.

The orange processing study meets the requirement of the 1995 JMPR for a citrus processing study that includes the main residues identified in the metabolism study.

From these processing factors and the STMR for whole oranges (0.065 mg/kg) the Meeting estimated an STMR for orange juice of 0.012 mg/kg and for dry orange pulp of 0.27 mg/kg.

Dry processed orange pulp is an animal feeding material that may represent 20% of the diet for dairy and beef cattle. The estimated maximum dietary burden of buprofezin for beef and dairy

cattle (on the basis of the estimated maximum residue level for oranges, 0.5 mg/kg, and the processing factor for dry pulp, 4.1) was equivalent to 0.45 ppm in the diet. The lowest feeding level in the dairy cow study was 5 ppm, which did not produce detectable levels of buprofezin in the tissues or milk, so the Meeting estimated maximum residue levels at or about the LOD for buprofezin residues in cattle milk (0.01* mg/kg), cattle meat (0.05* mg/kg), cattle kidney (0.05* mg/kg) and cattle liver (0.05* mg/kg), but could not recommend these maximum residue levels as being suitable for use as MRLs until the stabilities of the residues during freezer storage are confirmed.

The STMR for dry processed orange pulp is 0.27 mg/kg and the corresponding dietary burden for cattle, 0.059 ppm, is suitable for estimating STMRs for animal commodities.

The residues were below LOD in the muscle and kidney at the 5, 15 and 50 ppm feeding levels, and in the liver, fat and milk at the 5 and 15 ppm levels. Residues of buprofezin were detected in the fat and liver at the 50 ppm level and in milk fat at the 15 and 50 ppm levels. The Meeting noted that the dietary burden of 0.059 ppm was much less than the lowest feeding level where no residues were detected and, as an approximation for extrapolation, assumed proportionality between tissue level and dietary intake.

STMR (animal commodity) = LOD × (STMR dietary burden) ÷ (feeding level)

STMR for meat = 0.05 × 0.059 ÷ 50 = 0.00006 mg/kg (no detections at 50 ppm feeding level)

The same applies to kidney. For liver and milk there were no detections at the 15 ppm feeding level, so calculated STMRs are 0.0002 and 0.00004 mg/kg respectively. The Meeting regarded these calculated values as effectively zero and estimated STMRs of 0 mg/kg for meat, kidney, liver and milk, but the STMRs would not apply until MRLs are recommended.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue and STMR levels listed below. The maximum residue level is recommended for use as MRLs.

Definition of the residue (for compliance with MRLs and for estimation of dietary intake): buprofezin.

The residue is fat-soluble.

Commodity		MRL, mg/kg		STMR
CCN	Name	New	Previous	mg/kg
JF 0004	Oranges, Sweet, Sour	0.5	0.3 T[1]	0.011
	Orange juice			0.012
	Orange pulp, dry			0.27

[1]Withdrawal recommended by 1995 JMPR

FURTHER WORK OR INFORMATION

Desirable

Information is needed on the freezer storage stability of residues in animal commodities to validate the dairy cow feeding study. The Meeting was informed that the results of a 1-year freezer storage stability study for milk, fat and liver would be available in the year 2000.

DIETARY RISK ASSESSMENT

Chronic intake

A revised MRL for buprofezin in oranges has been recommended in addition to previous recommendations. STMR levels have been estimated for oranges and some processed commodities. The other values (2) used for the intake estimation are previously established CXLs.

The dietary intake of buprofezin is presented in Annex III. Estimated dietary intakes for buprofezin for the 5 GEMS/Food regional diets were in the range of 2-10% of the ADI. The Meeting concluded that intake of buprofezin resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The Meeting concluded that an acute RfD for buprofezin is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard, and residues are therefore unlikely to present an acute risk to consumers.

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CARBOFURAN (096)

EXPLANATION

Carbofuran was evaluated for residues by the 1997 JMPR in the CCPR Periodic Review Programme. At the 31st (1999) Session of the CCPR it was asked (ALINORM 99/24A, para79) whether the recommendations for MRLs for sorghum and sweet corn should be asterisked (*).

The 1999 CCPR also noted (ALINORM 99/24A, para 79) that, although the 1997 JMPR had concluded that an MRL for citrus fruits should be established for carbofuran and carbosulfan, only an MRL for oranges (sweet, sour) had been recommended. It was requested that an MRL for mandarin be elaborated.

APPRAISAL

Asterisk

The recommendations by the 1997 JMPR were 0.1* mg/kg for sorghum and 0.1 mg/kg for sweet corn (corn-on-the-cob).

In all sorghum residue trials used for estimating maximum residue levels, the residue was <0.01 mg/kg (the estimated limit of detection) and so it is safe to say that no residues were present. However, since the practical limit of determination in plant commodities is 0.1 mg/kg the Meeting agreed to maintain the current recommendation of 0.1* mg/kg for sorghum.

In the residue trials on sweet corn used for estimating maximum residue levels the residues were <0.03–0.08 mg/kg (n = 16, 10 residues >0.03 mg/kg). In this case residues were clearly present. Therefore, although the proposed MRL of 0.1 mg/kg is at the practical limit of determination, it should not be asterisked. The Meeting confirmed the 1997 recommendation of an MRL of 0.1 mg/kg for sweet corn (corn-on-the-cob).

MRL for mandarin

There is no registered use of carbofuran on citrus fruit, so all carbofuran residues arise from the use of carbosulfan. There are registered uses of carbosulfan on oranges in Mexico and Brazil and on oranges and mandarins in Spain. The supervised trials used by the 1997 JMPR to estimate a maximum residue level were mainly with oranges, some with mandarins (6 of about 28 trials). The residues in mandarins were comparable to those in oranges. The Meeting agreed to maintain the current recommendation for an MRL of 0.5 mg/kg for carbofuran in sweet and sour oranges and recommended the same MRL for carbofuran in mandarins. The STMR of 0.1 mg/kg for oranges was also extended to mandarins. The residue is defined as the sum of carbofuran and 3-hydroxycarbofuran, expressed as carbofuran. A group MRL for citrus fruits cannot be recommended since registered uses are solely on oranges and mandarins.

Residues in the edible pulp. Residues of carbosulfan, carbofuran and 3-hydroxycarbofuran were determined separately in the peel, pulp and whole fruit in several trials reported in the 1997 evaluation of carbosulfan. Five of the trials showed residues in the pulp, with a mean ratio of pulp to fruit residue of 0.0726. Since the highest residue of carbofuran + 3-hydroxycarbofuran found in the whole fruit was 0.5 mg/kg and the estimated STMR was 0.1 mg/kg, the corresponding residues in the pulp were estimated as 0.0363 mg/kg and 0.00726 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue and STMR levels shown below. The maximum residue level is recommended for use as an MRL.

Definition of the residue (for compliance with MRLs and for the estimation of dietary intake): sum of carbofuran and 3-hydroxycarbofuran, expressed as carbofuran.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FC 0206	Mandarin	0.5		0.1

DIETARY RISK ASSESSMENT

Chronic intake

An STMR for mandarins was added to the extensive list of STMRs estimated by the 1997 Meeting (Annex III).

International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on estimated STMRs, were in the range of 7-30% of the ADI. The Meeting concluded that the intake of residues of carbofuran resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The International Estimate of Short Term Intake (IESTI) for carbofuran was calculated as described in Section 3 of this report for commodities for which MRLs were recommended and STMRs estimated and for which consumption data (large portion consumption, unit weight) were available. The results are shown in Annex IV. The IESTI ranged from 3.5×10^{-4} to 6.3×10^{-4} mg/kg bw in the total population and from 1.35×10^{-3} to 2.58×10^{-3} mg/kg bw in children. As no acute reference dose has been established, the acute risk assessment for carbofuran was not finalized.

CARBOSULFAN (145)

EXPLANATION

Carbosulfan was evaluated for residues by the 1997 JMPR in the Periodic Review Programme. At the 31st (1999) Session of the CCPR it was noted (ALINORM 99/24A, para 79) that, although the 1997 JMPR had concluded that an MRL for citrus fruits should be established for carbofuran and carbosulfan, only an MRL for oranges (sweet, sour) had been recommended. It was requested that an MRL for mandarin be elaborated if it is considered to be more appropriate to recommend MRLs for individual commodities.

APPRAISAL

Carbofuran is a main metabolite of carbosulfan, as well as being itself a pesticide. Residues of carbosulfan are defined as carbosulfan, and residues of carbofuran are defined as the sum of carbofuran and 3-hydroxycarbofuran, expressed as carbofuran. The 1997 JMPR recommended MRLs for oranges (sweet, sour) of 0.1 mg carbosulfan/kg and 0.5 mg carbofuran/kg.

The 1997 JMPR recommended an MRL of 0.1 mg/kg and estimated an STMR of 0.01 mg/kg for carbosulfan in whole oranges (sweet, sour). A total of 53 samples gave a highest residue of 0.08 mg/kg in whole oranges. A ratio of 0.0726 was estimated for pulp : whole fruit residues from five trials which gave rise to residues in the pulp. The highest residue in the edible portion was therefore estimated as 0.08 mg/kg x 0.0726 = 0.0058 mg/kg, and the STMR in the edible portion was estimated as 0.01 mg/kg x 0.0726 = 0.00726 mg/kg.

There is no registered use of carbofuran on citrus fruit so all carbofuran residues arise from the use of carbosulfan. There are registered uses of carbosulfan on oranges in Mexico and Brazil and on oranges and mandarins in Spain. The supervised trials used by the 1997 JMPR to estimate a maximum residue level were mainly with oranges, some with mandarins (6 of about 28 trials). The residues in mandarins were comparable to those in oranges. The Meeting agreed to maintain the current recommendations for MRLs of 0.1 mg carbosulfan/kg and 0.5 mg carbofuran/kg for oranges (sweet, sour) and recommended in addition MRLs of 0.1 mg carbosulfan/kg and 0.5 mg carbofuran/kg for mandarin. A group MRL for citrus fruits cannot be recommended since registered uses of carbosulfan are solely on oranges and mandarins.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue and STMR levels shown below. The maximum residue level is recommended for use as an MRL.

Definition of the residue (for compliance with MRLs and for the estimation of dietary intake):

carbosulfan.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FC 0206	Mandarin	0.1		0.01

DIETARY RISK ASSESSMENT

Chronic intake

An STMR for mandarins was added to the STMR for oranges estimated by the 1997 Meeting (Annex III).

International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on estimated STMRs, were all 0% of the ADI. The Meeting concluded that the intake of residues of carbosulfan resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The International Estimate of Short Term Intake (IESTI) for carbosulfan was calculated as described in Section 3 of this report for commodities for which MRLs were recommended and STMRs estimated and for which consumption data (large portion consumption, unit weight) were available. The results are shown in Annex IV. The IESTI ranged from 5×10^{-5} to 9×10^{-5} mg/kg bw in the total population and from 2.1×10^{-4} to 4×10^{-4} mg/kg bw in children. As no acute reference dose has been established, the acute risk assessment for carbosulfan was not finalized.

CLETHODIM (187)

EXPLANATION

Clethodim was evaluated by the JMPR in 1994 and 1997. Numerous MRLs were recommended in the first evaluation, but questions were raised at the 1996 CCPR on quantitative aspects of the metabolism study on plants and both the quantities and nature of the goat metabolites. The basis for the limit of determination in animal tissues and the resulting recommendations for MRLs for several animal commodities were also questioned. Specific doubts were expressed in relation to the limit of determination achieved by a compound-specific method and the practical limit of determination claimed for routine monitoring and enforcement.

The manufacturer submitted data on new residue trials on alfalfa, artichokes, cabbages, field peas, lupins, carrots, cauliflower, clover, celery, flax, garlic, cucumbers, leeks, lentils, lettuce, onions, peaches, peppers, spinach, summer squash and tomatoes for the 1997 evaluation. Some of the trials were not reviewed as they were not indicated as required or desirable in the 1994 evaluation, and some did not address the questions raised at the 1996 CCPR. The 1997 JMPR recommended withdrawal of the draft MRLs for beans, sunflower seed and sunflower seed oil (crude and edible).

At the 1999 CCPR, comments were made in relation to the MRLs recommended for cattle meat and cattle offal based on the limits of determination in animal tissues. In addition, it was noted that there was no justification given for the recommended animal commodity MRLs with respect to levels found in animal feed commodities. It was suggested that the JMPR should provide an estimation of the exposure of livestock to residues in treated feed items, to confirm the appropriateness of the animal commodity MRLs.

For the current evaluation, the manufacturer reported new supervised trials on cucumbers, peppers, potatoes, sunflowers and dry beans, and processing studies on cotton, canola (rape seed), peanuts, sugar beets, soya beans, sunflowers and tomatoes. New information on physical and chemical properties and on formulations was provided, and revision of the previously reported specific analytical method was submitted with new validation data. Previously reviewed studies on metabolism in crops, rats, goats and hens and degradation in soil were re-submitted.

IDENTITY

Physical and chemical properties

Pure active ingredient

Solubility in buffer solutions	pH	g/l
	3.7	0.0181 (Willemsz-Geeroms, 1985)
	4.9	0.0718
	5.8	0.479
	6.6	1.74
	7.8	5.4
	8.8	12.4 (cloudy solution, colliodal suspension)
	8.9	10.4 14.8 (cloudy solution, colliodal suspension)

Technical material (Ashworth, 1988)

Colour:	amber
Physical state:	viscous liquid

Odour:	no characteristic odour
Melting point:	liquid at ambient temperatures
Boiling point:	decomposes below boiling point
Density:	1.1395 g/ml at 20°C (Willemsz-Geeroms, 1986)
Solubility:	soluble in most organic solvents, acetone, hexane, ethyl acetate. DMF: >90 g/100 ml at 25°C (Hance, 1988)
pH:	4.15 (1% w/v solution) (Knight, 1986).
Flammability:	flash point 78°C (closed cup, ASTM D-56) (Updyke, 1990)
Stability in sunlight:	half-life 16.3 hours at 23.8°C (Lam, 1987)
Storage stability:	half-life 8.4, 1.2 and 0.7 months at 20°C, 38°C and 50°C respectively. (Jackson, 1988)
Minimum purity:	88% clethodim
Main impurities:	trione 0.7% maximum; alkoxyamine 0.1% maximum

Formulations

EC 12.5% ai; EC 25% ai, manufacturing use product 37and 70% ai

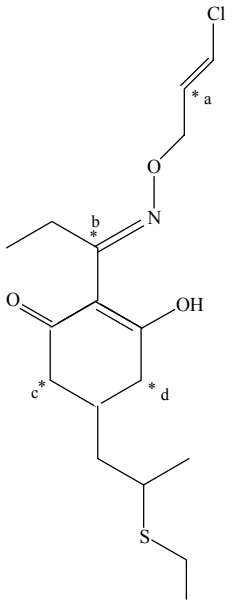
METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Metabolism studies on rats, a lactating goat and laying hens were re-submitted. The goat study (Rose and Suzuki, 1988) was reviewed in 1994 and 1997, and studies on the rat (Rose and Griffis, 1988) and hens (Lee, 1988) in 1994.

The metabolism studies were with [^{14}C]clethodim labelled in the 1-propyl position for goats, the 4- and 6-hydroxycyclohexenone ring for hens and the 4- and 6-ring and 2-allyl carbons for carrots, soya beans and cotton. The positions of the labels are shown in Figure 1.

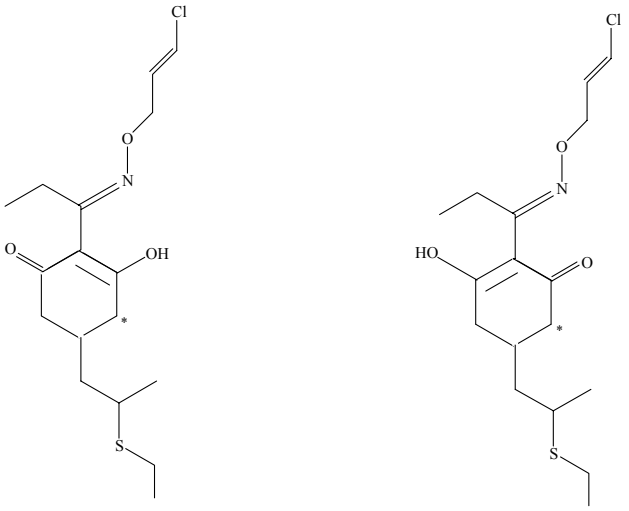
Figure 1.



a: 2-allyl; b: 1-propyl; c, d: 6- and 4- positions of hydroxycyclohex-2-enone ring

The labels in the ring positions are present as a 50/50 mixture owing to keto-enol tautomerism, Figure 2.

Figure 2.



The data from the studies on the goat and hens are repeated below to allow comparison of the distribution of radioactivity in the two species.

Table 1. Distribution of ^{14}C in a lactating goat (Rose & Suzuki, 1988) and laying hens (Lee, 1988).

Species	Dose regime	Sample	^{14}C, % of dose	Reference
Goat	1.16 mg/kg bw/day	Urine	56.43	Rose & Suzuki 1988
	for 3 days	Faeces	34.40	
		Milk	0.11	
		Blood	0.22	
		Tissues	0.37	
Total			91.53	
Hen	2.1 mg/kg bw/day	Excreta	77.9	Lee 1988
	for 5 days	Eggs	0.1	
		Tissues	1.9	
Total			79.9	
Hen	51.3 mg/kg bw/day	Excreta	84.7	Lee 1988
	for 5 days	Eggs	0.3	
		Tissues	4.2	
Total			89.2	

Most of the administered radioactivity was excreted: 90.94% of the dose by the goat and 77.9% and 84.7% of the low and high doses respectively by the hens. Most of the ^{14}C in the goat tissues was extractable with acetonitrile, with some in the methanol/water and hexane extracts and unextracted solids (Table 2). Peritoneal fat was the only substrate which was not easily extractable.

Table 2. Extraction of ^{14}C from goat tissues by various solvent systems.

Sample	% of ^{14}C in sample and (mg/kg clethodim equivalents)				
	Hexane	CH_3CN	MeOH-H_2O	Solids	Total
Liver	1.6 (0.007)	61.8 (0.256)	13.8 (0.057)	15.5 (0.064)	92.7 (0.384)
Kidney	1.1 (0.004)	80.4 (0.304)	9.3 (0.035)	6.7 (0.025)	97.5 (0.369)
Fat, subcutaneous	3.6 (0.003)	81.1 (0.064)	10.7 (0.008)	3.5 (0.003)	98.4 (0.078)
Fat, peritoneal	0.6 (0.000)	0.2 (0.000)	1.6 (0.000)	1.5 (0.000)	3.9 (0.002)
Muscle, hindquarter	0.7 (0.000)	81.8 (0.028)	10.8 (0.004)	6.8 (0.002)	99.3 (0.034)
Muscle, forequarter	1.4 (0.000)	80.1 (0.026)	8.6 (0.003)	8.1 (0.003)	98.2 (0.033)
Heart	10.1 (0.006)	76.6 (0.044)	5.3 (0.003)	6.0 (0.003)	98.0 (0.057)
Blood	1.1 (0.002)	85.7 (0.145)	6.5 (0.011)	4.6 (0.008)	97.9 (0.164)

The levels of clethodim and metabolites in tissues, organs and blood of the goat were tabulated in the 1997 monograph and the Table is repeated here for convenience. In milk, the radioactivity was associated with the *S*-methyl sulfoxide (5.5%), clethodim sulfoxide (~20%) and lactose derivatives (30-50%).

Table 3. Distribution of clethodim and metabolites in goat tissues, organs and blood after dosing at 1.16 mg/kg body weight/day with [^{14}C]clethodim.

Compound	% of ^{14}C in sample and (mg/kg as clethodim)						
	Liver	Kidney	Fat, subcutaneous	Muscle, forequarter	Muscle, hindquarter	Heart	Blood
Clethodim	27.6 (0.114)	1.3 (0.005)	2.8 (0.002)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	28.0 (0.047)
Clethodim sulfoxide	33.2 (0.137)	36.9 (0.139)	47.2 (0.037)	51.6 (0.017)	40.7 (0.014)	43.2 (0.025)	39.9 (0.067)
Clethodim sulfone	3.2 (0.013)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	3.8 (0.006)
S-methyl sulfoxide	6.2 (0.025)	30.8 (0.116)	29.0 (0.023)	28.5 (0.009)	32.4 (0.011)	37.2 (0.021)	11.6 (0.019)
Imine sulfoxide	1.5 (0.006)	4.1 (0.016)	4.7 (0.004)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	3.0 (0.005)
5-OH sulfone	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	0.0 (0.000)	2.7 (0.004)
Unidentified	4.0 0.016)	9.8 (0.037)		0.0 (0.000)	7.9 (0.003)	0.0 (0.000)	3.2 (0.005)
Total	75.7	82.9	91.8	80.1	81.0	80.4	92.2

The major compound in all the samples was clethodim sulfoxide, accompanied mainly by clethodim in the liver and blood and by the *S*-methyl sulfoxide in the other samples. The imine sulfoxide was present at levels in the range of about 1.5-5% in the liver, kidneys, fat and blood.

The distribution of the radioactivity in extracts of hen tissues and eggs is shown in Table 4 and its distribution among the labelled compounds in each sample in Table 5, after treatment at the high dose of 51.3 mg/kg body weight/day for 5 days.

Table 4. Distribution of extracted radioactivity in hen tissues and eggs.

Sample	% of ^{14}C in sample and (mg/kg clethodim equivalents)			
	CH_3CN	Hexane	Solids	Total recovered
Liver	83.6 (0.57)	ND	17.0 (0.11)	100.6
Kidney	94.5 (1.13)	1.7 (0.02)	11.4 (0.14)	107.6
Skin	83.3 (0.28)	1.6 (ND)	6.2 (0.02)	91.6
Fat	1002. (0.06)	0.7 (ND)	1.6 (ND)	102.5
Thigh	87.0 (0.14)	1.1 (ND)	7.4 (ND)	95.4
Breast	87.8 (0.03	0.1 (ND)	10.6 (ND)	98.5
Heart	80.6 (0.23)	3.1 (0.01)	13.5 (0.04)	97.2
Gizzard	111.5 (0.19)	1.5 (ND)	11.9 (0.02)	124.9
Egg yolk*	97.0 (0.03)	ND	14.1 (0.01)	111.1
Egg white*	96.3 (0.16)	ND	4.8 (0.01)	101.1

*Total from samples collected for 5 days
ND = not detectable.

Table 5. Distribution of clethodim and metabolites in hen tissues, organs and eggs after dosing at 51.3 mg/kg bw/day for 5 days.

Sample	% of ^{14}C in sample and (mg/kg clethodim equivalents)				
	Clethodim	Clethodim sulfoxide	Clethodim sulfone	Unidentified*	At origin
Liver	2.5 (0.41)	30.9 (5.00)	26.8 (4.34)	12.1 (2.17)	1.8 (0.28)
Kidney	4.6 (1.18)	39.5 (10.23)	25.1 (6.49)	11.3 (2.91)	3.3 (0.86)
Skin	6.3 (0.20)	47.5 (2.95)	27.8 (1.72)	10.1 (0.62)	1.0 (0.06)
Fat	33.5 (1.61)	41.3 (1.98)	15.7 (0.75)	5.0 (0.24)	1.8 (0.08)
Thigh	0.5 (0.03)	43.5 (2.22)	33.2 (1.69)	15.2 (0.77)	1.4 (0.07)
Breast	1.2 (0.05)	47.3 (2.13)	33.6 (1.51)	3.8 (0.17)	0.5 (0.02)
Heart	0.5 (0.05)	37.3 (3.50)	27.9 (2.62)	11.8 (1.10)	2.8 (0.26)
Gizzard	5.8 (0.40)	30.3 (2.60)	33.2 (2.26)	9.0 (0.62)	1.4 (0.09)
Egg white					
Day 0	5.9 (0.05)	65.9 (0.58)	9.9 (0.09)	12.4 (0.11)	4.3 (0.04)
Day 1	10.1 (0.83)	44.7 (3.68)	26.6 (2.18)	9.7 (0.80)	1.2 (0.10)
Day 2	4.5 (0.43)	47.2 (4.48)	36.3 (3.44)	3.1 (0.30)	1.7 (0.16)
Day 3	5.1 (0.39)	44.6 (3.42)	18.5 (1.42)	26.6 (2.86)	1.2 (0.10)
Day 4	4.2 (0.37)	39.4 (3.47)	10.7 (0.94)	38.0 (3.35)	2.6 (0.22)
Egg yolk **					
Day 1	19.7 (0.15)	33.9 (0.26)	29.1 (0.22)	3.4 (0.09)	0.9 (0.01)
Day 2	14.8 (0.20)	28.2 (0.39)	18.7 (0.26)	19.8 (0.27)	2.4 (0.03)
Day 3	20.2 (0.40)	29.0 (0.57)	21.3 (0.42)	4.4 (0.08)	2.2 (0.04)
Day 4	22.2 (0.56)	25.0 (0.63)	17.8 (0.45)	6.1 (0.16)	1.5 (0.04)

*Composite of multiple TLC bands
** Insufficient yolk sample on day 0 for analysis

Clethodim sulfoxide was the main radioactive residue in all samples except gizzard. Clethodim sulfone was generally the next most prominent, but was exceeded by clethodim in the fat and in one sample of yolk.

Goat liver and kidneys were analysed for clethodim and metabolites by the residue enforcement method described in the 1994 evaluation (King, 1984). The samples were extracted with MeOH. The MeOH was removed *in vacuo* and the residue partitioned with hexane and CH_3CN. In the liver samples 79.9% of the ^{14}C was found in the CH_3CN and 0.9% in the hexane, and in the kidneys 91.6% in the CH_3CN and 0.2% in the hexane. Aliquots of the CH_3CN phases were concentrated to dryness, transferred to MeOH/H_2O (1:2) and oxidized for analysis. Radioactivity was measured in the remaining CH_3CN fractions after separation by TLC and HPLC. The results of the GLC and total ^{14}C determination were as shown below.

Residue expressed as	Liver, mg/kg		Kidney, mg/kg	
	Enforcement	^{14}C	Enforcement	^{14}C
Clethodim	0.196	0.270	0.173	0.160
S-methyl sulfoxide	0.120	0.025	0.094	0.116
5-OH sulfone	0	0	0	0

Clethodim and its sulfoxide and sulfone residues in hen breast muscle from another study in which birds were dosed at 2.1 mg/kg bw were also determined by the enforcement method. The results from the GLC analysis gave 0.12 mg/kg as compared with the total ^{14}C analysis of 0.07 mg/kg.

Plant metabolism

Metabolism studies on carrots, soya beans and cotton plants were reviewed in 1994 and 1997 (Chen, 1988a,b). The distribution and characterization of the radioactivity after treatment with ring- and allyl-labelled [^{14}C]clethodim were detailed in the 1997 monograph. The predominant components of the radioactive residue were clethodim sulfoxide and/or the imine sulfoxide. Data from the two studies are shown in Tables 6 and 7.

Table 6. Distribution of ^{14}C in plants treated with [^{14}C]clethodim (Chen, 1988a,b).

Crop	Treatment	PHI, days	Sample	% of total ^{14}C in plant	
				ring label	allyl label
Carrots	2 × 0.28 kg ai/ha at 10.2-15.2 cm long leaves at 14 day interval	20	Leaves Roots	97.3 2.7	89.3 10.7
Cotton	2 × 0.28 kg ai/ha at 8-12 leaf stage at 14 day interval	70	Leaves Stems Shell Fibre (cotton) Seeds Roots	93.2 2.6 3.6 0.1 0.2 0.3	85.0 6.0 4.7 1.3 1.3 1.7
Soya beans	2 × 0.28 kg ai/ha at 6-8 leaf stage at 14 day interval	30	Leaves Stems Roots Pods Beans	83.8 0.8 0.2 5.1 10.1	78.4 1.2 0.6 5.6 14.2

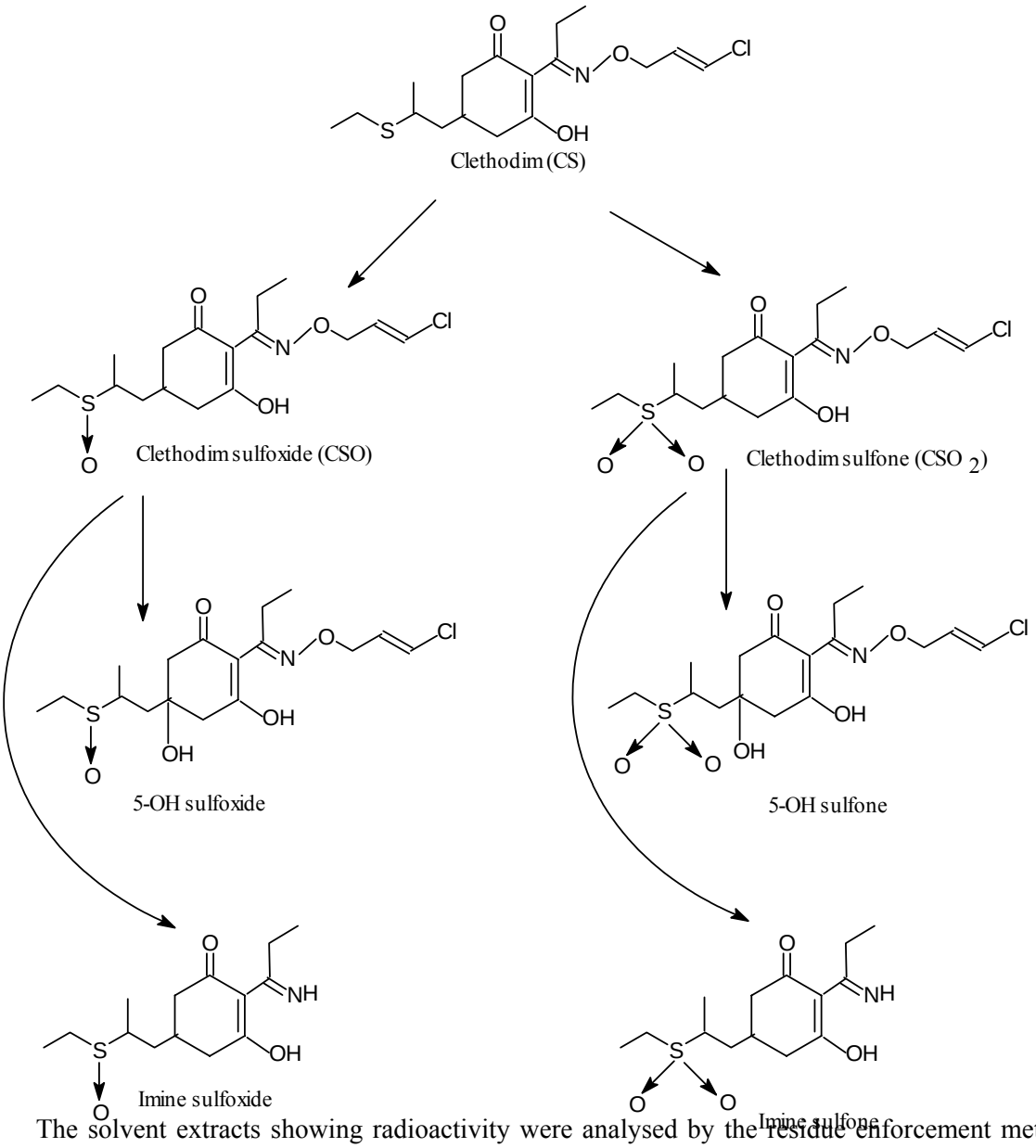
The roman numerals in Table 7 refer to the 4,6-hydroxycyclohexenone label and the italic numerals to the 2-allyl label.

Table 7. Distribution of ^{14}C residues in leaves and roots or seeds of treated crops.

Compound	^{14}C in samples and (mg/kg as clethodim)					
	Carrot leaves	Carrots	Soya bean leaves	Soya beans	Cotton leaves	Cotton seed
Clethodim		0.8 (0.003) *1.1 (0.007)*				
Clethodim sulfoxide	15.7 (3.50) *10.5 (0.97)*	28.6 (0.110) *33.9 (0.210)*	5.9 (1.65) *4.5 (0.79)*	32.0 (1.240) *31.5 (1.340)*	4.1 (0.55) *5.3 (0.35)*	4.3 (0.003) *3.1 (0.007)*
Clethodim sulfone	0.6 (0.13) *1.8 (0.17)*	3.4 (0.014) *4.6 (0.029)*	0.9 (0.25) *0.9 (0.16)*	4.6 (0.178) *5.1 (0.217)*	0.4 (0.05) *1.8 (0.12)*	2.8 (0.002) *0.4 (0.001)*
Imine sulfoxide	22.1 (4.93) ––––	9.9 (0.040) ––––	13.9 (3.88) ––––	7.8 (0.302) ––––	17.8 (2.40) ––––	6.0 (0.004) ––––
Imine sulfone	5.9 (1.32) ––––	8.6 (0.034) ––––	8.7 (2.43) ––––	8.1 (0.314) ––––	4.1 (0.55) ––––	2.3 (0.001) ––––
5-OH sulfoxide	1.6 (0.36) *1.0 (0.09)*	6.4 (0.026) *7.3 (0.045)*	trace *1.4 (0.25)*	7.1 (0.275) *4.0 (0.170)*	1.4 (0.19) *1.1 (0.07)*	0.6 (0.002) *0.4 (0.001)*
5-OH sulfone	1.9 (0.42) *1.7 (0.16)*	7.6 (0.030) *10.1 (0.063)*	3.1 (0.86) *2.2 (0.39)*	10.7 (0.414) *10.1 (0.429)*	0.4 (0.05) *0.6 (0.04)*	1.6 (0.001) *0.6 (0.001)*
Aromatic sulfone	0.3 (0.07) *0.6 (0.06)*	1.4 (0.006) *0.8 (0.005)*	0.5 (0.14) *0.4 (0.07)*	1.5 (0.058) *1.9 (0.081)*	0.5 (0.07) *0.4 (0.03)*	
Clethodim sulfoxide conj.	8.5 (1.90) *2.9 (0.27)*	5.9 (0.024) *8.3 (0.052)*	24.8 (6.92) *26.7 (4.70)*	8.5 (0.329) *11.5 (0.489)*	2.7 (0.37) *10.1 (0.67)*	
Clethodim sulfone conj.	0.5 (0.11) *4.3 (0.40)*	0.5 (0.002) *4.3 (0.027)*	2.0 (0.56) *12.3 (2.17)*	1.3 (0.050) *2.5 (0.106)*	1.3 (0.18) *5.0 (0.33)*	
Polar conj.	26.8 (5.98) *31.6 (2.91)*	10.2 (0.041) *13.4 (0.083)*	18.3 (5.11) *31.4 (5.53)*	9.9 (0.383) *4.3 (0.183)*	31.5 (4.25) *56.2 (3.75)*	29.5 (0.020) *28.9 (0.064)*
Unextracted	5.3 (1.18) *9.3 (0.86)*	3.7 (0.015) *11.9 (0.074)*	8.9 (2.48) *12.2 (2.15)*	1.5 (0.058) *8.9 (0.378)*	4.6 (0.62) *12.2 (0.81)*	46.3 (0.032) *61.0 (0.134)*

Similar trends were observed for both labels. The main identified components of the radioactive residue were generally clethodim sulfoxide and/or its conjugates. The imine sulfoxide was prominent in the leaves. Much of the residue was characterized only as polar conjugates or, particularly in cotton seed, as unextracted.

Figure 3. Proposed metabolic pathways of clethodim in plants.



The solvent extracts showing radioactivity were analysed by the residue enforcement method (King, 1984). The total extractable residue in the plant samples was oxidized and methylated, and the residues were determined as dimethyl 3-[2-(ethylsulfonyl)propyl]pentanedioate (DME) and the corresponding 5-hydroxy compound (DME-OH). The reaction sequence for DME is shown in Figure 4. TLC and autoradiography methods were used in place of GLC to quantify DME and DME-OH. A comparison with the total extractable ^{14}C residues, quantified as DME and DME-OH, is shown below. The comparison is also shown for soya beans determined in a separate experiment.

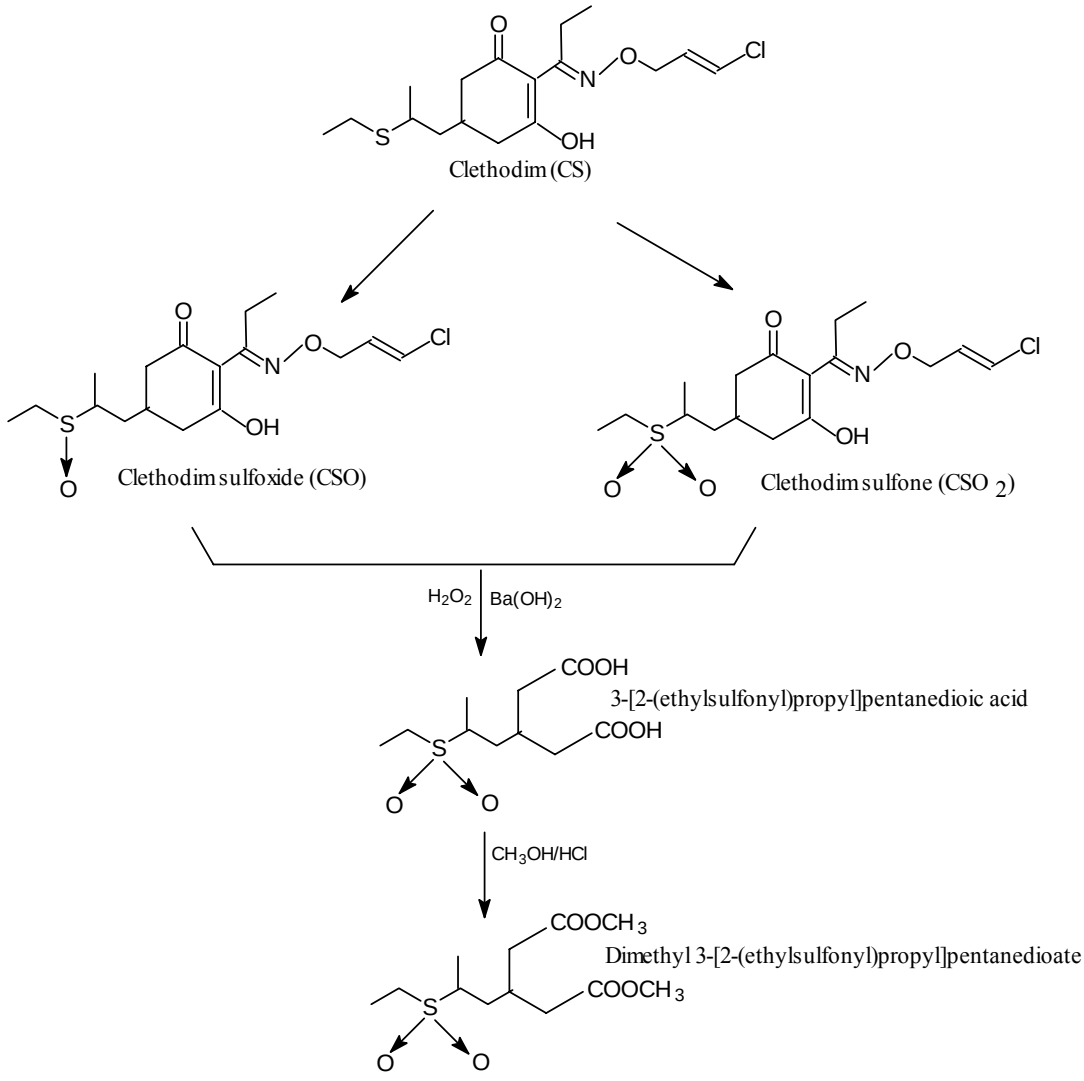
Sample	% of ^{14}C in sample as total radioactivity and as DME and DME-OH			
	^{14}C	DME	^{14}C	DME-OH
Soya bean leaves	67	62	2	3
Soya beans	46	56	18	18
Carrot leaves	48	56	3	4
Carrots	66	60	31	15
Cotton leaves	34	32	3	2
Cotton seeds	53	29	9	4

Soya beans	DME (expressed as mg/kg clethodim)	DME-OH (expressed as mg/kg clethodim)
Residue enforcement method	38.1	20.5
^{14}C as calculated*	39.9	19.3

* Calculated as sum of DME- and DME-OH-producing residues, *i.e.* sum of clethodim sulfoxide and sulfone, imine sulfoxide and sulfone, conjugates of clethodim sulfoxide and sulfone.

Figure 4. Reaction sequence in non-specific regulatory analytical method (POAST) to form DME.

(5-hydroxy-clethodim sulfoxide and sulfone are converted to the corresponding 3-hydroxy-substituted pentanedioate DME-OH).



The comparison between the calculated ^{14}C residues expressed as clethodim and the residues determined by the enforcement method (sum of DME and DME-OH expressed as clethodim) shows that the enforcement method is capable of determining all the metabolites which are included in the residue as defined. The verification with soya beans using the standard enforcement method confirms this capability.

It was noted that the values for DME and DME-OH in the verification were reported as corrected for recovery. The recoveries of DME and DME-OH were 73% and 53% respectively, from fortification with clethodim and the 5-OH sulfone at 10 μg/g.

Environmental fate in soil

Several studies of degradation in or on soil previously submitted by the manufacturer were reviewed in the 1994 monograph. These included studies of aerobic and anaerobic degradation (Pack, 1988a,b, 1990) and photodegradation (Chen, 1988c,d). A new study of degradation and an investigation of the adsorption and desorption of clethodim are described below.

In a degradation study (Cosgrove, 1993), clethodim, clethodim sulfoxide and clethodim sulfone were added to sterilized and unsterilized loam soil and their degradation monitored for 60 days. Soil was collected from a test site in a canola-growing region in Canada and sterilized by autoclaving at 121°C for an hour. Unsterilized soil was refrigerated at 6°C until ready for use. The loam contained 42% sand, 47% silt and 11% clay, with pH 6.3, 9.5% organic carbon, and 68.6 meq/100 g cation exchange capacity. Test samples were fortified with about 1 mg/kg each of clethodim, clethodim sulfoxide and clethodim sulfone and maintained under aerobic conditions in the dark at temperatures of 6°C or 21°C. Samples were taken for chemical and microbial analysis at 0, 1, 3, 7, 14, 30 and 60 days after fortification. Clethodim and its derivatives were quantified by HPLC-MS; a limit of detection of 0.01 mg/kg was reported for each compound.

Clethodim was rapidly converted to clethodim sulfoxide in both sterile and non-sterile soils, and was detected only on day 0 in non-sterile soil, and on days 0 and 1 in sterile soil at both temperatures. The concentration of clethodim sulfoxide reached maximum levels after 7 days in sterile and non-sterile soils at 6°C and sterile soil at 21°C. In non-sterile soil at 21°C, maximum levels of clethodim sulfoxide were found 1 day after treatment. Maximum levels of clethodim sulfone in non-sterile soil were observed after 30 days at 6°C and 7 days at 21°C. Clethodim sulfone was not formed in the sterile soil at either temperature, indicating that microbial activity is responsible for its formation in loamy soil.

The calculated half-life of clethodim sulfoxide was 30 days in sterile soil and 17 days in non-sterile soil at 6°C, and 26 days and 8 days respectively at 21°C. Again, the degradation of clethodim sulfoxide was rapid in non-sterile soils at 21°C.

The calculated half-lives of clethodim sulfone were 45 and 18 days at 6°C and 18 and 12 days at 21°C in sterile and non-sterile soil respectively. Comparison of the half-lives and rate constants of the sulfoxide and sulfone indicated that both compounds are degraded at twice the rate in the non-sterile soil as in the sterile soil at both temperatures.

The recoveries of clethodim, clethodim sulfoxide and clethodim sulfone were 91-150%, 64-146% and 41-107% from soil fortified at 1, 0.96 and 0.88 mg/kg.

In a study of adsorption and desorption Pack (1988c) treated five soils with organic matter contents of 0.4-2.8% C with radiolabelled clethodim, clethodim sulfoxide, clethodim sulfone and clethodim oxazole sulfone. The soils were clay loam, loamy sand, silt loam, sand, and sandy clay loam. Clethodim and its sulfoxide and sulfone were labelled with ^{14}C in the 4 and 6 ring positions and the oxazole sulfone in the 5 and 7 positions.

In the adsorption phase of the study aliquots of solutions at 0.1, 0.2, 0.5 and 1 μg/ml in 0.01 M $CaCl_2$ were added to weighed samples of soil, the mixtures were shaken for an hour, then centrifuged and the supernatants analysed by HPLC. In the desorption phase fresh 0.01 M $CaCl_2$ was added to each soil and shaken again for an hour. The resulting supernatants were analysed by HPLC and the soils combusted for measurement of ^{14}C.

The calculated Freundlich adsorption and desorption constants (K_d) are given in Table 8.

Table 8. Adsorption and desorption constants of clethodim, clethodim sulfoxide, clethodim sulfone and clethodim oxazole sulfone.

Compound	Soil	K_d adsorption	K_d desorption
Clethodim	Clay loam	0.08	1.40
	Loamy sand	1.57	4.15
	Silt loam Sand	0.15 0.51	380.0 22.6
	Sandy clay loam	0.46	12.75
Clethodim sulfoxide	Clay loam	<0.2	
	Loamy sand	0.22	1.06
	Silt loam	<0.2	
	Sand	<0.2	
	Sandy clay loam	<0.2	
Clethodim sulfone	Clay loam	<0.1	
	Loamy sand	0.11	1.37
	Silt loam	<0.1	
	Sand	<0.1	
	Sandy clay loam	<0.1	
Clethodim oxazole sulfone	Clay loam	6.96	25.30
	Loamy sand	0.29	0.72
	Silt loam	1.79	3.30
	Sand	1.02	7.33
	Sandy clay loam	1.60	5.69

The results show that clethodim, clethodim sulfoxide and clethodim sulfone are weakly adsorbed and clethodim oxazole sulfone is weakly to moderately adsorbed by the soils tested.

Environmental fate in water/sediment systems

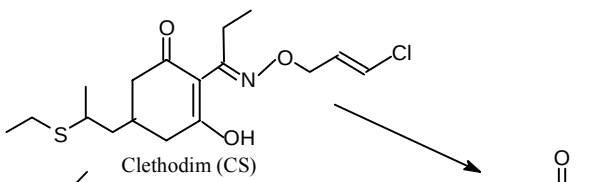
The photodegradation of clethodim in water was investigated in two studies by Chen (1988c,d). Buffered solutions at pH 5, 7 and 9 of [^{14}C]clethodim (10 mg/l) labelled in the cyclohexene ring or the allyl group were exposed to natural sunlight for up to 30 days and analysed at regular intervals by HPLC-MS. Control samples were maintained at 25°C in the dark and the experimental samples were exposed to natural sunlight in the presence and absence of acetone which functioned as a photosensitizer.

Calculated photolysis half-lives of the ring-labelled compound were 1.71, 6.84 and 9.57 days at pH 5, 7 and 9 respectively without acetone and 0.94, 1.22 and 0.52 days with acetone. The detected photoproducts were clethodim sulfoxide, imine sulfoxide, oxazole sulfoxide, oxazole, imine and imine ketone, and DME sulfoxide. After 30 days, the main products remaining were the imine sulfoxide and DME sulfoxide.

Photolysis half-lives of the allyl-labelled compound were 1.49, 4.05 and 6.0 days at pH 5, 7 and 9 respectively in the absence of acetone, and 0.20, 0.61 and 0.33 days respectively in its presence. These half-lives are shorter than those found with the ring labels, apparently owing to higher light intensity.

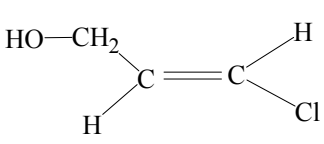
The photolytic mechanisms of transformation include oxidation at the ethylthio group, elimination of the chloroallyl side chain to form the imine and oxazole, with further oxidation to yield the DME sulfide and sulfoxide, and the oxazole sulfoxide. The allyl label showed chlorinated vinyl degradation products which decompose to CO_2

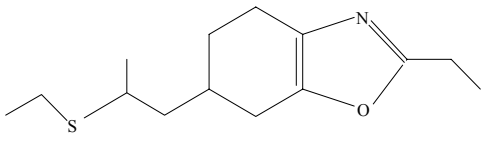
Figure 5. Proposed photolytic pathways of clethodim in water.



The hydrolysis of allyl- and propyl-labelled [^{14}C]clethodim was investigated in sterile water at pH 5, 7 and 9 at 25°C (Pack, 1988d). Solutions at 5 and 10 mg/l were incubated in the dark at 25°C and samples taken at 0, 1, 3, 7, 21 and 32 days were analysed by HPLC and GC-MS.

The HPLC chromatogram of clethodim showed two peaks. In solutions at pH 5 and 7 the ratio of the two peaks changed as a function of time. No significant change was observed at pH 9. The two peaks were interpreted as the (*E*)- and (*Z*)-oxime forms of clethodim, the (*E*)- form being less polar as it cannot form an internal H-bond between the oxime oxygen and the hydroxyl group of the cyclohexene ring. The rate of interconversion was fastest at pH 5, and not measurable in 30 days at pH 9. Two main degradation products were formed at pH 5, an oxazole and a hydroxyvinyl compound:





Cleavage of the vinyl group and ring closure to form the oxazole are the predominant mechanisms involved in the transformation of clethodim in sterile water.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods for the determination of clethodim and its metabolites in crops, chicken and beef tissues, milk, eggs, soil and aqueous solutions were provided. A non-specific method for the determination of clethodim residues in crops, chicken and beef tissues, milk and eggs reviewed in 1994 has since been revised (Lai, 1994a). The sample is extracted with MeOH and/or H_2O, and cleaned up by alkaline precipitation ($Ca(OH)_2$) and acidic back-extraction into CH_2Cl_2. Alkaline H_2O_2 oxidizes the ethylthio and sulfoxide groups to sulfone with oxidative cleavage to form dicarboxylic acids, which are converted to dimethyl esters (DME and DME-OH) with anhydrous MeOH and HCl and partitioned into CH_2Cl_2. After an optional clean-up on a silica gel column the esters are determined by GLC with a flame photometric detector in the sulfur mode. The total residues are expressed as clethodim. This method was used to determine the residues of clethodim and metabolites in the supervised residue trials detailed later.

In alfalfa trials in the USA (Lai, 1995a) reviewed in 1997 the original common moiety method (RM-26B-1) was used to determine total residues of clethodim, which were quantified as DME and DME-OH and summed as clethodim equivalents. The predominant component of the total residue was DME in most instances. Recoveries from forage and hay fortified with clethodim and 5-OH-clethodim sulfone at 0.05, 0.1, 0.2, 0.5, 1, 2 and 5 mg/kg of each compound were determined. Average recoveries from forage were 97% ± 23% (n = 57) for clethodim and 112% ± 20% (n = 57) for 5-OH-clethodim sulfone. Average recoveries from hay were 103 ± 33% (n = 51) for clethodim and 108% ± 29% (n = 52) for 5-OH-clethodim sulfone. Recoveries at the lowest fortifications of 0.05 mg/kg were 204 and 106% of clethodim and 5-OH-clethodim sulfone respectively from hay and 146 and 164 % from forage.

A compound-specific HPLC method, EPA-RM-26-D-3, for the determination of clethodim and its metabolites in crops, animal tissues, milk and eggs (Lai, 1996a) allows residues from the use of sethoxydim to be differentiated from those of clethodim. Residues of clethodim sulfoxide, clethodim sulfone, the 5-hydroxy sulfoxide and sulfone, and *S*-methyl-clethodim sulfoxide may be determined as enol methyl ethers. A chromatogram from a crop analysis was provided which showed the presence of clethodim, 5-hydroxy-clethodim sulfone, sethoxydim and 5-hydroxy-sethoxydim sulfone as four separate HPLC peaks. The method is a revised version of EPA-RM-26-D-1 (Lai and Ho, 1990) and its modification EPA-RM-26-D-2 (Lai and Fujie, 1993). These were reviewed in 1994 and 1997 respectively.

The method involves extraction with MeOH or MeOH/H_2O followed by alkaline precipitation. After partitioning with CH_2Cl_2, the residues are methylated with CH_2N_2, oxidized with *m*-chloroperbenzoic acid and cleaned up on a silica column. A base wash clean-up is included for crops and milk samples. The methylated sulfones of clethodim, 5-OH-clethodim and *S*-methyl-clethodim are determined by HPLC on a C-18 column with UV detection at λ = 266 or 254 nm. The limits of determination in various commodities ranged from 0.02 to 5 mg/kg, defined as the lowest fortification concentration giving acceptable recoveries. These are listed in Table 9.

Table 9. Limits of determination reported for the compound-specific method.

Commodity	Limit of determination (mg/kg)		
	CSO/CS	5-OH CSO_2	S-MeCSO
Eggs	0.05		
Liver	0.20		
Milk	0.02		0.02

Commodity	Limit of determination (mg/kg)		
	CSO/CS	5-OH CSO_2	S-MeCSO
Soya beans	0.05	0.05	
Onion	0.10	0.10	
Potato	0.20	0.20	
Tomato	0.20	0.02	
Alfalfa forage	1.0	1.0	
hay	5.0	5.0	
Sugar beet tops	0.25	0.10	
roots	0.10	0.10	
Peanut meat	0.20	0.20	
hay	0.20	2-3	
Dry bean seeds	0.20	0.20	

CSO	clethodim sulfoxide	CS	clethodim
5-OH CSO_2	5-hydroxy-clethodim sulfone	S-MeCSO	*S*-methyl-clethodim sulfoxide

The method allows recovery and quantification of the major metabolites likely to be present in crops, animal tissues, milk and eggs, and the limits of determination for clethodim and its sulfoxide in animal products were reported as 0.02 mg/kg in milk, 0.05 mg/kg in eggs and 0.2 mg/kg in hen liver. Representative chromatograms were provided for a crop and two chromatograms for animal extracts, one recorded before the method revision and the other after the revision.

A justification for the use of CH_2N_2 was provided, identical to that reported in 1997 (Rose, 1990).

Specialized methods for the determination of clethodim and its degradation products in soil and aqueous solutions were submitted. The method for aqueous solutions was reviewed in 1994.

The method reported by Ho (1989) describes the determination of clethodim, clethodim sulfoxide, clethodim sulfone, the oxazole sulfoxide and oxazole sulfone in soil. In brief, the analytical procedure involves extraction of soil with $MeOH/H_2O$, partitioning into hexane and CH_2Cl_2 and derivatization with CH_2N_2. After methylation the extract is washed with base, cleaned up on a silica column and analysed by HPLC with a UV detector at 254 nm. A C-18 column is used for clethodim and a C-4 column for the metabolites. The limit of detection for all the compounds is reported as 0.01 mg/kg.

The determination of clethodim and clethodim sulfoxide in aqueous solutions was described by Mitten (1990a,b). Samples are extracted with CH_2Cl_2, the solvent is evaporated and the remaining residue is dissolved in CH_3CN containing 2% v/v acetic acid. Clethodim is measured by HPLC with a UV detector at 247 nm. The limit of detection for clethodim and clethodim sulfoxide is reported as 0.01 mg/kg. The methods were reviewed in 1994 (referenced as Fujie,1990b).

Stability of pesticide residues in stored analytical samples

Data on the storage stability of clethodim and its metabolites in a number of crops and crop fractions were provided. These included alfalfa and its processed commodities, celery, clover, cotton, dry beans, dry onions and garlic, peanuts, soya beans, sunflowers, tomatoes, eggs, hen and cattle tissues, and milk.

The storage stability of clethodim, determined as the sum of DME and DME-OH, was investigated for up to 16 months in forage and 14 months in hay. The recoveries at each sampling are shown below.

Sample	Storage period, months	Recovery, %
Forage	15	69, 85, 92, 93
	16	75, 93

Sample	Storage period, months	Recovery, %
Hay	6.5	90, 141
	10.1	84, 109
	12.4	103, 136
	14.4	87, 118

The storage stability of clethodim residues in celery was reported by Lai (1996b) in connection with trials reported in Table 32 in the 1997 monograph. Samples of celery were fortified with clethodim, clethodim imine sulfone and 5-OH-clethodim sulfone at 2 mg/kg and stored as macerates for up to 739 days at -15°C to -25°C. The results are shown in Table 11. Analysis was by the revised non-specific enforcement method RM-26B-3 (Lai, 1994a); residues of clethodim and clethodim imine sulfone were determined as DME and residues of 5-OH-clethodim sulfone were determined as DME-OH.

Recoveries of clethodim and 5-OH-clethodim sulfone from celery fortified at 0.2, 0.5, 1.0, 2.0 and 5 mg/kg were acceptable, in the range 77-99% for clethodim and 62-107% for 5-OH-clethodim sulfone.

Table 10. Stability of clethodim and its metabolites in fortified celery macerates during frozen storage (Lai, 1996b).

Compounds added	Fortification level, mg/kg	Storage period, days	Recovery, %
Clethodim + clethodim imine sulfone	2 + 2	686	75, 77.0
		690	77, 79
		730	73. 67
		739	70, 74
5-OH-clethodim sulfone	2	686	26, 26
		690	40, 42
		730	54, 56
		739	55, 56

Recoveries of clethodim and clethodim imine sulfone from freshly fortified control samples of celery were unacceptably low (shaded areas in Table 10): 47.2 and 57.4% from the controls for 686 and 690 days storage and 30 and 39% from those for 730 days. The recovery of 5-OH-clethodim sulfone from freshly fortified samples was also low at 30, 47 and 57% for 686, 690 and 730-day controls. Only two recoveries of 88.2% for clethodim and 87.8% for 5-OH-clethodim sulfone can be considered within acceptable limits in freshly fortified samples. These were reference samples for the macerates stored for 739 days.

In a validation of a residue trial on clover (Lai, 1995/1996) macerated control samples were stored for 289-309 days at -15°C to -25°C after fortification with clethodim sulfoxide and 5-OH-clethodim sulfone. The results are shown in Table 11.

Table 11. Stability of clethodim metabolites in frozen fortified macerates of clover (Lai, 1995/1996).

Sample	Recovery, %		
	Storage period, days	Clethodim sulfoxide	5-OH-clethodim sulfone
Clover forage	289	84, 92	78, 87[1]
	309	70, 80	71, 59
Clover hay	297	84, 93	77, 86

[1] A fresh control sample was not fortified with 5-OH-clethodim sulfone.

Recoveries from freshly fortified samples were 63-112% of clethodim and 56-123% of 5-OH-clethodim sulfone 56-123% from forage, and 84-105% of clethodim and 62-89% of 5-OH-clethodim sulfone from hay.

Since the samples in the residue trial (1997 monograph, Table 36) were analysed after 250-254 days, the results show that the residues would have remained stable during the period between sampling and analysis.

The stability of incurred clethodim residues in cotton seed was determined by Lai (1988c). Treated samples were analysed within two months of harvest and fuzzy seed macerates were analysed 55, 110 and 172 days after storage at -20°C. The recoveries are shown in Table 12.

Table 12. Stability of incurred residues in cotton seed stored at -20°C (Lai, 1988c).

Storage period, days	Initial residues, mg/kg	Recovery, %
55	0.44	110, 116
	1.37	95
110	0.33	83, 87
	1.15	80
172	0.44, 0.5	116, 128
	1.33	92

Total clethodim residues were quantified as the sum of DME and DME-OH by Method RM-26A-1. Recoveries from macerates freshly fortified at 0.5 mg/kg with clethodim and 5-OH-clethodim sulfone were 85-96% and 88-129% respectively.

Untreated dry beans, vines and hay from residue trials (Lai, 1994c) were fortified with clethodim and 5-hydroxy-clethodim sulfone, stored at -20°C, and periodically re-analysed. The results are shown in Table 13.

Table 13. Stability of residues in fortified dry beans, vines and hay stored at -20°C.

Sample	Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
		CS	5-OH CSO_2	DME	DME-OH
Beans	0	89	106		
	135	73, 85	80, 89	102, 103	94, 114
	643	84	80	104, 119	81, 114
Vines, dry	0	79	81		
	126	83	104	83, 113	88, 106
	618	93	87	89, 95	94, 106
	637	85	81	156	97
	640	93	87	117	91
Hay	0	85	86		
	101	56	80	76, 78	86, 86
	430	76	89	99, 115	94, 110

CS: clethodim 5-OH CSO_2: 5-OH-clethodim sulfone

Recoveries of DME and DME-OH after storage are within acceptable limits and comparable to recoveries from freshly fortified samples analysed concurrently by Methods RM-26B-2 and RM-26B-3.

The storage stability in onions was investigated by Lai (1993). Untreated onion macerates were fortified with 0.5 mg/kg clethodim and 0.5 mg/kg 5-OH-clethodim sulfone, stored at -20°C, and analysed after 3, 6.6, 9.3 and 12.6 months of storage by the enforcement method RM-26B-1.

Table 14. Stability of clethodim and hydroxy-clethodim sulfone in fortified macerates of onions stored at -20°C.

Storage period, months	% recovery of clethodim	% recovery of sulfone
0	102, 110	108, 112
3	88, 90	98, 100
6.6	78, 82	94, 96
9.3	66, 80	82, 92
12.6	74, 80	92, 100

Recoveries from freshly fortified samples were 77-123% for clethodim and 89-112% for the sulfone. The results suggest a loss or degradation of clethodim of about 25% during the period of storage.

In connection with a processing study (Lai, 1994b), untreated macerates of peanut hay, vines and hulls were fortified with 0.5 mg/kg clethodim and 0.5 mg/kg 5-OH-clethodim sulfone and stored at −20°C for up to 390 days. Meal, presscake, crude oil, refined oil and soapstock were produced from field-treated nuts, and both fortified and treated samples were analysed at intervals after storage. Hydroxy-clethodim sulfoxide or sulfone residues were not initially present in peanut oil, so a laboratory-fortified sample was stored and analysed concurrently with the sample from treated nuts. The results are shown in Table 15.

Table 15. Stability of clethodim residues in macerates of peanuts and their processed commodities stored at -20°C.

Sample	Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
		CS	5-OH CSO_2	DME	DME-OH
Kernels*	0	90	92		
	149	109	104	82, 85	147, 185
	255	120	95	129, 130	293, 300
	395	94	112	97, 113	244, 247
Hulls	0	94,96	90, 98		
	104	107	92	66, 82	66, 92
	182	81	82	92, 104	70, 84
	282	72	79	82, 86	84, 86
	392	71	85	76, 78	74, 74
Vines	0	106, 108	82, 86		
	107	115	95	94, 100	74, 80
	185	77	109	100, 102	82, 90
	277	95	114	94, 94	99, 99
	378	79	98	78, 80	78, 78
Hay	0	105, 109	108, 111		
	104	**	107	98, 102	86, 92
	188	84	76	92, 102	80, 88
	286	93	102	90, 96	98, 104
	384	79	83	80, 84	90, 92
Meal	0	113	115		
	448	94	79	90	113
Soapstock	0	67	91		
	429	76	99	69	146
Crude oil	0	98	112		
	433	74	64	76	
	530	65	97	76	
Refined oil	0	80	94		
	433	66	65	78, 81	
	530	65	97	84	
Laboratory sample	0		96, 100		
	99		97		98, 102

* Recoveries were reported as corrected. ** Fortified with wrong concentration.
CS clethodim 5-OH CSO_2 5-OH-clethodim sulfone

The apparently higher recoveries from kernels after storage are explained as being due to the low initial levels of DME-OH.

Macerates of sugar beet roots and tops were fortified with clethodim and 5-OH-clethodim sulfone at 0.5 mg/kg and stored at -20°C for up to 11 months (Lai, 1991). Freshly fortified samples were analysed concurrently at each sampling. The results are shown in Table 16.

Table 16. Stability of clethodim and hydroxy-clethodim sulfone in fortified macerates of sugar beet tops and roots.

Sample	Storage period, days	% recovery of clethodim	% recovery of 5-hydroxy sulfone
Roots	0	103	114
	91	96, 98	104, 112
	200	74, 82	70, 92
	280	82, 92	90, 106
	346	76, 100	100, 100
Tops	0	80, 106	78, 98
	109	85, 88	98, 100
	189	66, 72	68, 76
	273	68, 70	76, 86

The residues in sugar beet roots were stable for 11 months but there was a slow loss from the tops of about 30% in 9 months. In the residue trial the samples of tops and roots were analysed within 9 and 10 months respectively. Recoveries from the freshly fortified samples were 73-106% for clethodim and 79-114% for the sulfone. The methods of analysis were RM-26A-1 and RM-26B-1.

Treated sunflower seeds were re-analysed after storage at -20°C for 97 days (Lai, 1996c); the results are shown in Table 17.

Table 17. Stability of incurred residues in sunflowers stored at -20°C.

Storage period, days	% recovery from fresh fortification		% recovery in stored sample	
	DME	DME-OH	DME	DME-OH
0	88	79		
97	104	74	93, 110	92, 81

The residues in the sunflower seeds were stable after storage for 97 days. In the residues trials the samples were extracted within 57 days after harvest.

Processed tomato commodities were either re-analysed after a period of storage at -20°C or fortified in the laboratory with clethodim and 5-OH-clethodim sulfone and re-analysed at intervals (Lai, 1995b). Freshly fortified samples were analysed concurrently with the stored samples. The results are shown in Tables 18 and 19 .

Table 18. Stability of incurred residues in dry tomato pomace stored at -20°C.

Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
	DME	DME-OH	DME	DME-OH
0	85	108		
86	81	86	78, 78	158, 158
126	95	96	139	151
345	95	96	148	139

Table 19. Stability of clethodim and hydroxy-clethodim sulfone in fortified macerates of processed tomato commodities stored at -20°C.

Sample	Storage period, days	% recovery from fresh fortification		% of initial residue in stored sample	
		CS	5-OH CSO_2	CS	5-OH CSO_2
Juice	0	90, 92	90, 92		
	153	84	86	52, 68	50, 58
	266	87	93	70, 72	66, 70
Paste	0	73, 74	70, 77		
	162	88	101	60, 66	78, 78
	274	75	87	64, 68	74, 78
Wet pomace	0	82, 96	93, 96		
	176	86	97	84, 86	80, 82
	266	83	92	84, 90	72, 78

There was a discernible loss of residues in tomato paste and juice after storage for 162 and 153 days. This loss was not apparent in the pomace. In the residue trials, samples of processed commodities were stored between 55 and 83 days before analysis by Method RM-26B-3.

Chicken tissues and eggs were fortified with clethodim, 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide at 1 and 2 mg/kg and stored up to 8 weeks at -13° to -29°C (Lear, 1989). The data were reviewed in the 1994 monograph and are shown in Table 20.

Table 20. Stability of clethodim and metabolites in fortified hen tissues and eggs at -13° to -29°C (Lear, 1989).

Sample	Storage period, weeks	Fortification level, mg/kg	Recovery, %		
			S-Me-CSO	CS	5-OH-CSO_2
Eggs	0	1	77, 65	83, 69	90, 75
	4	1	100, 120, 110	113, 121, 103	94, 102, 91
	8	2	110, 111, 112	112, 111, 109	107, 99, 104
Fat	0	1	69, 76, 71	68, 83, 76	69, 88, 80
	3	1	98, 104, 95	100, 105, 96	105, 113, 101
	6	1	91, 94, 98	99, 103, 103	90, 96, 94
Gizzard	0	1	70, 76, 77	76, 80, 84	82, 84, 85
	3	1	91, 97, 101	88, 95, 97	92, 94, 98
	6	1	100, 104, 94	102, 106, 96	86, 89, 84
Liver	0	1	76, 77, 78	84, 84, 82	84, 83, 84
	3	1	99, 103, 99	96, 99, 99	100, 102, 96
	6	1	100, 95, 87	102, 96, 85	91, 85, 83
Muscle	0	1	67, 63, 70	71, 68, 75	72, 70, 77
	3	1	99, 106, 100	99, 105, 98	99, 105, 100
	6	1	101, 99, 112	104, 105, 116	88, 74, 101

S-Me-CSO: S-methyl clethodim sulfoxide CS: clethodim 5-OH-CSO_2: 5-OH-clethodim sulfone

The three compounds were stable in chicken tissues and eggs after 6 or 8 weeks storage. Method RM-26A was employed to determine DME and DME-OH.

Samples of cattle tissues and milk from a feeding study were fortified with clethodim, 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide and stored at -20°C for up to 5 months (Weissenburger, 1989). Milk and tissue samples were fortified at 0.05 and 0.25 mg/kg respectively with each compound. Concurrent recoveries from freshly fortified samples were determined at each sampling. The results are shown in Table 21.

Table 21. Stability of clethodim and metabolites in fortified cattle tissues and milk at -20°C (Weissenburger, 1989).

Sample	Storage period, months	Fortification level, mg/kg	Recovery, %[1]		
			S-Me-CSO	CS	5-OH-CSO_2
Milk	0	0.05	98, 92	94, 91	117, 109
	1	0.05	88 (83, 91)	80 (78, 84)	102 (99, 107)
	3	0.05	79, 82 (46, 46)	73, 75 (41, 39)	86, 97 (44, 44)
	3.5	0.05	84, 89 (82, 90)	79, 83 (86, 89)	90, 95 (101, 103)
	4	0.05	78, 92 (76, 80)	74, 80 (72, 76)	91, 107 (94, 98)
	5	0.05	72, 114 (65, 87)	70, 94 (64, 78)	80, 116 (75, 92)
Fat	0	0.25	83, 85	79, 79	99, 107
	1	0.25	93, 96 (91, 91)	82, 83 (89, 101)	101, 106 (101, 118)
	2	0.25	78, 82 (82, 92)	71, 82 (87, 95)	82, 82 (88, 94)
	3	0.25	75, 82 (83, 91)	75, 77 (80, 89)	83, 88 (83, 90)
	4	0.25	89, 92 (77, 86)	80, 83 (62, 79)	98, 100 (87, 96)
	5	0.25	85, 97 (84)	78, 90 (78)	89, 104 (83)
Kidney	0	0.25	77, 90	77, 88	94, 113
	1	0.25	82, 85 (79, 80)	80, 84 (79, 85)	98, 98 (101, 109)
	2	0.25	67, 74 (80, 87)	69, 71 (80, 87)	81, 81 (87, 98)
	3	0.25	83, 87 (74, 84)	78, 81 (74, 78)	85, 85 (71, 74)
	4	0.25	79, 84 (76, 81)	79, 84 (75, 79)	95, 95 (82, 95)
	5	0.25	86, 93 (81, 94)	80, 82 (77, 88)	86, 91 (77, 86)
Liver	0	0.25	78, 78	70, 70	72, 79
	1	0.25	70, 70 (74, 79)	69, 71 (78, 79)	80, 97 (102, 102)
	2	0.25	75, 81 (80, 81)	65, 71 (78, 78)	79, 84 (79, 84)
	3	0.25	77, 87 (86, 89)	68, 76 (79, 82)	91, 103 (83, 83)
	4	0.25	75, 95 (75, 82)	75, 90 (73, 80)	93, 113 (84, 97)
	5	0.25	74, 87 (79, 98)	72, 82 (81, 98)	85, 89 (81, 101)
Muscle	0	0.25	88, 88	80, 80	91, 98
	1	0.25	89, 90 (90, 93)	73, 76 (83, 88)	94, 100 (88, 94)
	2	0.25	86, 92 (80, 94)	76, 80 (71, 92)	92, 97 (87, 97)
	3	0.25	86, 106 (74, 84)	74, 94 (72, 77)	103, 111 (74, 78)
	4	0.25	90, 92 (86, 89)	78, 79 (81, 83)	103, 110 (99, 103)
	5	0.25	95, 99 (86, 95)	76 (82, 76)	98, 98 (91, 94)

S-Me-CSO: *S*-methyl-clethodim sulfoxide CS: clethodim 5-OH-CSO_2: 5-OH-clethodim sulfone
[1]Values in parentheses are concurrent recoveries from freshly fortified samples

There was no discernible degradation of clethodim or the metabolites in the tissues or milk during the study.

Definition of the residue

The current definition is "sum of clethodim and its metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulfoxides and sulfones, expressed as clethodim". Metabolism studies on carrots, cotton, soya beans, hens and a lactating goat confirm that the current definition is appropriate.

USE PATTERN

Registered uses on potatoes, cucumbers, dry beans, peppers and sunflowers are shown in Table 23. Use patterns on numerous crops were tabulated in the 1994 and 1997 monographs and are not repeated here. GAP for potatoes was reported by the Canadian government.

Table 22. Registered use patterns of clethodim on cucumbers, dry beans, peppers, potatoes and sunflowers.

Crop	Country	Form.	Application			PHI, days
			Method	Rate, kg ai/ha	No.	

Crop	Country	Form.	Application			PHI, days
			Method	Rate, kg ai/ha	No.	
Cucumbers	Chile	240 g/L	Spray	0.096-0.48		
	Ecuador	240 EC	Spray	0.06-0.12		
	New Zealand	240 EC	Spray	0.06-0.72		35
	Paraguay	2 EC	Spray	0.096-0.24		
	Poland	240 EC	Spray	0.096-0.24		
	USA[1]	2 EC	Spray	0.11-0.28	2	14
	Venezuela	2 EC	Spray	0.12-0.24		
Dry beans	Belize	24 EC		0.072-0.24		
	Bolivia	240 EC		0.072-0.24		65
	Brazil	240 EC		0.084-0.108		40
	Bulgaria	240 EC		0.096-0.192		
	Costa Rica	24 EC		0.072-0.24		
	Dominican Republic	24 EC		0.06-0.12		7-10
	El Salvador	24 EC		0.072-0.24		
	Guatemala	24 EC		0.072-0.24		
	Nicaragua	24 EC		0.072-0.24		
	Peru	240 EC		0.12-0.18		15
	Turkey	240 EC		0.096-0.192		60
	Uruguay[2]	240 EC		0.084-0.168		65
	USA	2 EC		0.11-0.28		30
Peppers	Chile	240 g/L		0.096-0.48		
	Ecuador	240 EC		0.06-0.12		
	New Zealand	240 EC		0.06-0.72		35
	Paraguay	2 EC		0.096-0.24		
	USA[1]	2 EC		0.11-0.28		20
	Venezuela	2 EC		0.12-0.24		
Potatoes						
	Canada	240 EC		0.09		60
Sunflowers	Argentina	240 EC		0.096-0.336		100
	Bolivia	240 EC		0.072-0.24		65
	Bulgaria	240 EC		0.096-0.192		
	Canada	240 EC		0.045-0.09	2	72
	Croatia	240 EC		0.096-0.24		
	France	240 EC		0.18-0.48		100
	Hungary	240 EC		0.072-0.288		
	Israel	240 EC		0.084-0.12		
	Paraguay	2 EC		0.096-0.24		
	Spain	240 EC		0.096-0.192	2	
	Ukraine	12.5 EC		0.048-0.216	1	
	Uruguay[2]	240 EC		0.084-0.168	1	65
	USA[1]	2 EC		0.11-0.28		70
	Venezuela	2 EC		0.12-0.24		

[1] Pending
[2] Proposed label

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data were provided from supervised trials on potatoes, cucumbers, beans, peppers (sweet and hot) and sunflowers. Some of the data were reviewed in 1994 and/or 1997 and are repeated here for convenience. The trials are reviewed in the crop sequence of the *Codex Alimentarius Classification of Foods and Animal Feeds*. GAP for each crop is tabulated with the residue data for ease of comparison.

Residues, application rates and spray concentrations have been rounded to 2 significant figures, or for residues near the limit of detection to 1 significant figure. Although the trials included control

plots, no residues in the untreated samples are reported unless they exceeded the limit of determination. Residues from trials according to GAP are underlined; those used to estimate STMRs are double-underlined. All residues, unless otherwise stated, are defined as *sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulfones, expressed as clethodim.* The analytical method used is included in the footnotes to each Table. The limit of determination is indicated at the bottom of each Table or in the text if reference is made to the validation of a specific method.

Potatoes. The results of supervised residue trials in Canada were reviewed in 1994 and 1997. Select 240 EC was applied at 15 cm height (flowering to early petal fall) to potato crops at the maximum label rate (0.09 kg ai/ha; 1% v/v adjuvant) and twice that rate. Samples were collected 45 and 60 days after treatment; the registered PHI is 60 days. The trials were conducted in 6 States in 12 representative growing areas of Canada. The results are shown in Table 23.

Table 23. Residues in potatoes from supervised field trials in Canada. Tubers analysed. Ref. 92-001.D.

Location	Application			PHI,	Residues, mg/kg		Total,
year, (variety)	Form	kg ai/ha	No.	days	DME	DME-OH	mg/kg
Ontario, 1990,	240 EC	0.09	1	46	<0.05	<0.05	<u><0.1</u>
(Superior)					<0.05	<0.05	<0.1
Ontario, 1990	240 EC	0.09	1	46	0.057	0.053	0.11
(Superior)					0.070	0.071	<u>0.141</u>
Ontario, 1990	240 EC	0.09	1	46	<0.05	<0.05	<u><0.1</u>
(Kennebec))					<0.05	<0.05	<0.1
Nova Scotia,	240EC	0.09	1	45	<0.05	<0.05	<u><0.1</u>
1990, (Kennebec)					<0.05	<0.05	<0.1
Ontario, 1990,	240 EC	0.09	1	61	<0.05	<0.05	<u><0.1</u>
(Superior)					<0.05	<0.05	<0.1
Ontario, 1990,	240 EC	0.09	1	61	0.066	0.071	<u>0.137</u>
(Superior)					0.059	0.062	0.121
					<0.05	<0.05	<u><0.1</u>
					<0.05	<0.05	<0.1
Ontario, 1990,	240 EC	0.09	1	60	<0.05	<0.05	<u><0.1</u>
(Kennebec)					<0.05	<0.05	<0.1
Ontario, 1990,	240 EC	0.18	1	46	<0.05	<0.05	<0.1
(Superior)					<0.05	<0.05	<0.1
Ontario, 1990,	240 EC	0.18	1	46	0.127	0.126	0.253
(Superior)					0.097	0.107	0.204
Ontario, 1990,	240 EC	0.18	1	46	0.109	0.095	0.204
(Kennebec))					0.073	0.101	0.174
Nova Scotia,	240 EC	0.18	1	45	0.068	0.060	0.128
1990, (Kennebec)					<0.05	<0.05	<0.1
Ontario, 1991,	240 EC	0.09	1	45	<0.05	<0.05	<u><0.1</u>
(Sebago)							
Ontario, 1991,	240 EC	0.09	1	45	<0.05	<0.05	<u><0.1</u>
(Red Chieftain))					<0.05	<0.05	<0.1
PEI, 1991,	240 EC	0.09	1	44	<0.05	<0.05	<0.1
(Russet Burbank)					<0.05	<0.05	<0.1
Quebec, 1991,	240 EC	0.09	1	46	0.119	0.125	0.244
(Kennebec)					0.242	0.221	<u>0.463</u>
Quebec, 1991,	240 EC	0.09	1	46	0.164	0.162	<u>0.326</u>
(Superior)					0.1	0.108	0.208
Manitoba,	240 EC	0.09	1	45	0.160	0.114	0.274
1991, (Norland)					0.199	0.149	<u>0.348</u>
Saskatchewan)	240 EC	0.09	1	45	<0.05	<0.05	<u><0.1</u>
1991, Norland)					<0.05	<0.05	<0.1
Alberta, 1991,	240 EC	0.09	1	44	<0.05	<0.05	<u><0.1</u>
(Shepody)					<0.05	<0.05	<0.1
Ontario, 1991,	240 EC	0.09	1	60	<0.05	<0.05	<u><0.1</u>

Location year, (variety)	Application Form	kg ai/ha	No.	PHI, days	Residues, mg/kg DME	DME-OH	Total, mg/kg
(Sebago)							
Ontario, 1991,	240 EC	0.09	1	60	<0.05	<0.05	<0.1
(Red Chieftain)					<0.05	<0.05	<0.1
PEI, 1991,	240 EC	0.09	1	59	<0.05	<0.05	<0.1
(Russet Burbank(					<0.05	<0.05	<0.1
Quebec, 1991,	240EC	0.09	1	60	0.106	0.126	0.232
(Kennebec)					0.087	0.098	0.185
Quebec, 1991,	240 EC	0.09	1	60	0.127	0.127	0.254
(Superior)					0.173	0.166	0.339
Manitoba, 1991,	240 EC	0.09	1	60	0.109	0.081	0.190
(Norland)					0.097	0.088	0.185
Saskatchewan,	240 EC	0.09	1	59	<0.05	<0.05	<0.1
1991, (Norland)					<0.05	<0.05	<0.1
Alberta, 1991,	240 EC	0.09	1	60	<0.05	<0.05	<0.1
(Shepody)					<0.05	<0.05	<0.1
Ontario, 1991,	240 EC	0.18	1	45	<0.05	<0.05	<0.1
(Sebago)					0.069	0.062	0.131
Ontario, 1991,	240 EC	0.18	1	45	0.054	0.051	0.105
(Red Chieftain,					<0.05	<0.05	<0.1
PEI, 1991,	240 EC	0.18	1	44	<0.05	0.05	<0.1
(Russet Burbank)					0.067	0.065	0.132
Quebec, 1991,	240 EC	0.18	1	46	0.441	0.406	0.847
(Kennebec)					0.325	0.300	0.625
Quebec, 1991,	240 EC	0.18	1	46	0.334	0.256	0.590
(Superior)					0.292	0.262	0.554
Manitoba, 1991,	240 EC	0.18	1	45	0.096	0.075	0.171
(Norland)					0.288	0.223	0.511
Saskatchewan,	240 EC	0.18	1	45	<0.05	<0.05	<0.1
1991, (Norland)					<0.05	0.05	<0.1
Alberta, 1991,	240 EC	0.18	1	44	0.065	0.073	0.138
(Shepody)					0.083	0.063	0.152
Ontario, 1991,	240 EC	0.18	1	60	<0.05	0.057	<0.17
(Sebago)					<0.05	<0.05	<0.1
Ontario, 1991,	240 EC	0.18	1	60	0.061	0.050	0.111
(Red Chieftain)					<0.05	<0.05	<0.1
PEI, 1991,	240 EC	0.18	1	59	<0.05	<0.05	<0.1
(Russet Burbank)					<0.05	0.05	<0.1
Quebec, 1991,	240 EC	0.18	1	60	0.272	0.296	0.568
(Kennebec)					0.251	0.269	0.520
Quebec, 1991,	240 EC	0.18	1	60	0.325	0.321	0.646
(Superior)					0.396	0.349	0.745
Manitoba, 1991,	240EC	0.18	1	60	0.163	0.110	0.273
(Norland)					0.200	0.132	0.332
Saskatchewan,	240EC	0.18	1	59	<0.05	<0.05	<0.1
1991, (Norland)					<0.05	0.05	<0.1
Alberta, 1991,	240 EC	0.18	1	60	<0.05	<0.05	<0.1
(Shepody)					<0.05	0.05	<0.1
GAP Canada	**240 EC**	**0.09**	**1**	**60**			

The common moiety method RM-26A-1 was used and recoveries of clethodim sulfoxide and 5-OH-clethodim sulfone were determined at 0.05, 0.1, 0.5 and 1 mg/kg. The range of recoveries at each concentration is shown below. The limit of detection of DME and DME-OH was 0.05 mg/kg.

Fortification level, mg/kg	Recovery, %	
	CSO	5-OH CSO_2
0.05	66-105 (n = 11)	69-113 (n = 11)
0.1	66-86 (n = 3)	63-87 (n = 3)
0.5	61-77 (n = 4)	60-75 (n = 4)
1.0	66, 69	68, 69

Total clethodim residues ranged from <0.1 to 0.46 mg/kg in trials which were in accord with the registered use pattern.

Cucumbers. Supervised trials on cucumbers were conducted in Poland and the USA. The data were reviewed in 1997. The US data were generated as part of an IR-4 program‡ and two sprays of clethodim were applied with a 14-day interval. In the Polish trial clethodim was applied at the 4-6 leaf stage of growth.

Table 24. Residues in cucumbers from trials in the USA and Poland.

Country, year, (variety)	Application			PHI, days	Residues, mg/kg		Reference
	Form.	kg ai/ha	No.		DME	DME-OH	
USA, (Florida), 1994		0.28	2	14	<0.14	<0.13	5219.94-FL47
USA, (New York), 1994		0.28	2	14	<0.14	<0.13	5219.94-NY10
USA, (Michigan), 1994		0.28	2	13	<0.14	<0.13	5219.94-MI15
USA, (Wisconsin), 1994		0.28	2	14	<0.14	<0.13	5219.94-WI13
USA, (Sth Carolina), 1994		0.28	2	13	<0.14	<0.13	5219.94-SC*08
USA, (Texas), 1994		0.28	2	14	<0.14	<0.13	5219.95-TX*21
Poland, 1995	240 EC	0.24[1]	1	35 38	<0.05, <0.05, <0.05 <0.05, <0.05, <0.05		Report 1995
GAP **Poland**	**240 EC**	**0.1**[2] **0.24**[3]	**1** **1**	**35** **35**			

[1]Application at 4 to 6 leaf stage of growth.
[2]Annual monocotyledonous weeds.
[3]Couch grass.

Although the US results are listed, registration for the use of clethodim on cucumbers is pending.

Cucumbers were fortified with clethodim sulfoxide and 5-OH-clethodim sulfone at 1.12 and 0.99 mg/kg respectively and stored for 518 and 526 days at -12 to -22°C. Residues were determined as DME and DME-OH and expressed as clethodim. The recoveries are shown below.

Storage period, days	Recovery, %	
	Clethodim sulfoxide	5-OH clethodim sulfone
518	75, 91	89, 101
526	89, 93	96, 98

Recoveries in the US validation of the method were determined by fortification with clethodim sulfoxide and 5-OH-clethodim sulfone at 0.11 and 0.10 mg/kg respectively. Recoveries were 95-117% for clethodim sulfoxide and 87-94% for 5-OH-clethodim sulfone determined as DME and DME-OH.

Recoveries from cucumbers in the US trials were checked by fortification with clethodim sulfoxide at 0.116 and 1.16 mg/kg and 5-OH-clethodim sulfone at 0.09 and 0.92 mg/kg. Recoveries were 88-118% for clethodim sulfoxide and 89-116% for 5-OH-clethodim sulfone. In the Polish trials, the limit of detection was reported as 0.05 mg/kg, with recoveries at 0.1 and 1 mg/kg of 76-88% and 84-92% respectively.

Dry beans. The results of trials in Brazil and the USA are presented in Table 26. The Brazilian trials were reviewed in 1994 and 1997 and are tabulated for comparison with the new data. In the US trials two applications were made at 13-15 day intervals at rates of 0.28 or 0.29 kg ai/ha. Samples of dry

‡ IR-4 = Interregional Research Project No. 4, which is the USDA Minor Use Program.

beans, vines and hay were collected at intervals after treatment. Recoveries in the US trials are reported in Table 13 as analyses at day 0.

Table 25. Residues in dry beans from trials in Brazil and the USA. The US trials were by Lai (1994c).

Country, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
Brazil, 1989/1990	240 EC	0.108	2	45	bean	<u><0.5</u>	61479 A/79119[1]
				65		<0.5	
	240 EC	0.216	2	45	bean	<0.5	
				65		<0.5	
Brazil, 1990	240 EC	0.084	1	25	bean	0.37	Chevron Brazil [2]
				45		<u>0.06</u>	
				65		<0.05	
				85		<0.05	
		0.108	1	25	bean	0.48	
				45		<u>0.07</u>	
				65		<0.05	
				85		<0.05	
		0.168		25	bean	0.82	
				45		0.11	
				65		<0.05	
				85		<0.05	
		0.216		25	bean	0.93	
				45		0.14	
				65		<0.05	
				85		<0.05	

Country, year (variety)	Application			PHI,	Sample	Residues, mg/kg		Total,
	Form	kg ai/ha	No.	days		DME	DME-OH	mg/kg
USA (Michigan), 1993,	2 EC	0.28-0.29	2	30 + 5*	bean	0.76	0.22	<u>0.98</u>
(Sierra)						0.74	0.20	0.94
					hay, dry	0.81	0.49	<u>1.3</u>
						0.82	0.46	1.3
				15	vines, dry	0.95	0.26	<u>1.2</u>
						1.0	0.24	1.2
USA (Nth Dakota), 1993 (Pearl Navy)	2 EC	0.28	2	30 + 1*	bean	0.55	0.25	0.80
						0.59	0.22	<u>0.81</u>
					hay	1.8	0.32	2.1
						1.9	0.41	<u>2.3</u>
				15	vines, dry	2.3	0.51	<u>2.8</u>
						2.2	0.54	2.7
USA (California), 1993, (Henderson Bush Lima)	2 EC	0.28	2	30 + 7*	bean	<0.1	<0.1	<u><0.1</u>
						<0.1	<0.1	<0.1
					hay	<0.1	<0.1	<u><0.1</u>
						<0.1	<0.1	<0.1
				15	vines, dry	<0.1	<0.1	<u><0.1</u>
						<0.1	<0.1	<0.1
USA (Idaho), 1993,	2 EC	0.28	2	30 + 15*	bean	0.40	0.24	<u>0.64</u>
(UI 537 Pink)						0.39	0.25	0.64
					hay	2.4	0.37	2.8
						2.9	0.39	<u>3.3</u>
				15	vines, dry	1.8	<0.1	<u>1.8</u>
						1.7	0.14	1.8
USA (Michigan), 1992, (Albion)	0.94 EC	0.28	2	30 + 1*	bean	0.47	0.32	<u>0.79</u>
						0.37	0.21	0.58
					hay	0.67	0.59	1.3
						0.73	0.65	<u>1.4</u>
				15	vines, dry	0.77	0.33	1.1
						1.2	0.33	<u>1.5</u>
USA (Nth Dakota), 1992 (Upland)	0.94 EC	0.28	2	30 + 4*	bean	1.1	0.47	<u>1.6</u>
						1.1	0.46	1.6
					hay	0.72	0.61	1.3

Country, year (variety)	Application			PHI,	Sample	Residues, mg/kg		Total,
	Form	kg ai/ha	No.	days		DME	DME-OH	mg/kg
						1.1	0.91	2.0
				24	vines, dry	0.88	0.46	1.3
						1.0	0.48	1.5
USA (Colorado), 1992, (Pinto)	0.94 EC	0.28	2	30 + 9*	bean	0.69	0.45	1.1
						0.44	0.28	0.72
					hay	3.7	1.8	5.5
						2.7	1.3	4.0
				15	vines, dry	1.8	0.31	2.1
						1.9	0.34	2.2
USA (California), 1992, (Dark Red Kidney)	0.94 EC	0.28	2	30 + 7*	bean	1.1	0.33	1.4
						1.0	0.21	1.2
					hay	1.1	0.14	1.2
						1.3	0.16	1.5
				30	vines, dry	0.22	<0.1	0.22
						0.23	<0.1	0.23
USA (Nebraska), 1992,	0.94 EC	0.28	2	30 + 2*	bean	0.79	0.25	1.0
(Great Northerns Navy)						0.86	0.26	1.1
					hay	1.3	0.26	1.6
						1.5	0.28	1.8
				15	vines, dry	1.5	0.26	1.8
						1.6	0.21	1.8
GAP								
Brazil	**240 EC**	**0.084-0.108**		**40**				
USA	**2 EC**	**0.105-0.28**	**1-2**	**30**				

***** Drying time after harvest.
[1] Two sprays at the 4-7 leaf stage (10 cm plants) and at flowering (30-40 cm plants); plot size 9 m^2, soil pH 3.6, C 3.1%, 'argiloso' soil. Limit of detection 0.5 mg/kg; recovery of clethodim 93 and 52%, clethodim sulfoxide 90 and 69%, at 0.5 mg/kg. Method RM-26A.
[2]Post-emergent application with 0.5% v/v crop oil. Limit of detection 0.05 mg/kg. Recoveries of clethodim, clethodim sulfoxide and 5-OH-clethodim sulfone 110, 75%; 100, 78% and 100, 76% respectively.

Peppers (sweet and hot). Trials in Italy and the USA were reported (Table 27). The Italian trial was reviewed in 1994. Details are given as footnotes to Table 26. In the two US trials, two applications were made at 12- to 18-day intervals.

Table 26. Residues in peppers from trials in Italy and the USA.

Country, year (variety)	Application			PHI,	DME	DME	Residues,	Reference
	Form.	kg ai/ha	No.	days		-OH	mg/kg	
Italy (Latina), 1990, (Heldor)	240 EC	0.24	1	18			0.08, 0.116	0266-90 [1]
				28			0.03, 0.075	
				38			0.041, 0.049	
Bell peppers								
USA (Georgia), 1993	0.94 EC	0.28	2	20	0.11	<0.1	0.11	Lai, 1995 [2]
					0.14	<0.1	0.14	5226.93-GA802
USA (Texas), 1993	0.94 EC	0.28	2	21	0.17	0.12	0.29	5226.93-TX*02
					0.20	0.14	0.34	
USA (California), 1994	0.94 EC	0.28	2	NA	0.49	0.13	0.62	5226.94-CA*96
					0.43	0.15	0.58	
USA (Florida), 1993	0.94 EC	0.28	2	21	0.36	0.18	0.54	5226.93-FL17
					0.34	0.17	0.51	

Country, year (variety)	Application			PHI,	DME	DME	Residues,	Reference
	Form.	kg ai/ha	No.	days		-OH	mg/kg	
USA (Nth Carolina), 1993	0.94 EC	0.28	2	19	0.32 0.27	0.13 0.11	0.45 0.38	5226.93-NC01
USA (New York), 1993	0.94 EC	0.28	2	19	0.60 0.46	0.29 0.22	0.89 0.68	5226.93-NY01
Non-bell peppers								
USA (Georgia), 1993	0.94 EC	0.28	2	20	0.12 0.12	<0.1 <0.1	0.12 0.12	Lai, 1995 5335.93-GA*03
USA (Texas), 1993	0.94 EC	0.28	2	21	0.2 0.21	0.18 0.18	0.40 0.39	5355.93-TX*0.3
USA (California), 1993	0.94 EC	0.28	2	NA	0.62 0.56	0.29 0.26	0.91 0.82	5355.94-CA*95
USA (Florida), 1993	0.94 EC	0.28	2	21	0.25 0.28	0.18 0.20	0.43 0.48	5355.93-FL18
USA (New Jersey), 1993	0.94 EC	0.28	2	22	0.60 0.59	0.32 0.28	0.92 0.87	5355.93-NJ02
GAP USA (pending)		0.11-0.28	1-2	20				

[1] Limit of detection 0.03 mg/kg. Residues determined as sum of DME and DME-OH, expressed as clethodim. Recoveries at 0.03 mg/kg 94, 94, 94%.
[2]Method RM-26B-3. Limit of detection 0.1 mg/kg. Recoveries at 0.1, 0.2 and 0.5 mg/kg: clethodim sulfoxide (as DME) 76-131% (n = 15), average 100%; 5-OH-clethodim sulfone (as DME-OH) 74-145% (n = 15), average 101%.
[3]Method RM-26-B-3. Limit of detection 0.1 mg/kg; recoveries of clethodim sulfoxide (as DME) at 0.2, 0.5 and 1mg/kg 69-102% (n = 9), average 92%; 5-OH-clethodim sulfone (as DME-OH) at 0.2, 0.5, 0.6 and 1.3 mg/kg 69-129% (n = 9), average 89%.

Data from the US trials are listed although registration is only pending.

Sunflowers. The trials were in Argentina, Canada, France, Italy and the USA. In the USA, Select Herbicide was applied twice at a rate of 0.28 kg ai/ha with a 14-day re-treatment interval, the first application 30-40 days after emergence and the second about 70 days before harvest. The samples collected were mature clean seed in the hull, dried to less than 14% moisture. In one trial in North Dakota, Select was applied at 5 times the pending maximum label rate and the seeds were processed into oil and meal; the results are shown in Table 45.

Data from one French trial were in summary form with no field details (Tomen, 1988). In two other French trials (Tomen France, 1997, 1998) Select 240 EC was applied at the maximum label rate of 0.5 kg ai/ha at the 6-8 leaf stage or before flowering. Only total residues were reported in two of the trials.

In the Canadian trials, clethodim was applied at 1 and 2 times the maximum label rate and the crops were harvested 72-96 days after treatment.

Table 27. Residues in sunflower seeds and products from supervised trials in Argentina, Canada, France, Italy and the USA.

Country, year, (variety)	Application			PHI, days	Sample	DME	DME-OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
Argentina, (Salto), 1987,	2 EC	0.12 0.24	1 1	108 108	seeds seeds	0.06 <0.05	<0.05 <0.05	0.06 <0.05	T7009 [1]
Argentina, (Salto), 1986	2 EC	0.12 0.24	1 1	102 102	seeds seeds	<0.05 0.085	<0.05 <0.05	<0.05 0.085	T7010 [2]
Argentina, (Buenos Aires), 1987	2 EC	0.12 0.24	1 1	99 99	seeds seeds hulls	<0.05 0.16 0.10	<0.05 <0.05 0.09	<0.05 0.16 0.19	T7011[3]

Country, year, (variety)	Application			PHI, days	Sample	DME	DME-OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
					extracted presscake	0.17	0.17	0.34	
					expelled presscake	0.15	0.15	0.30	
					refined oil	<0.05	<0.05	<0.05	
					crude oil	<0.05	<0.05	<0.05	
					extracted crude oil	<0.05	<0.05	<0.05	
					processed seed	0.08	0.09	0.17	
Argentina, (Santa Fe), 1987	2 EC	0.12	1	106	seeds	<0.05	<0.05	<0.05	T7012 [4]
		0.24	1	106	seeds	0.065	<0.05	0.065	
USA, (Illinois), 1995	0.94 EC	0.28	2	56	seeds	0.35	0.39	0.74	V-11186A[5]
(Pioneer)						0.33	0.40	0.73	
USA, (Minnesota), 1995	0.94 EC	0.27-0.28	2	66	seeds	2.8	1.2	4.0	V-11186-B
(Sigco 458)						3.1	1.3	4.4	
USA, (Nebraska), 1995	0.94 EC	0.28	2	69	seeds	0.31	0.39	0.70	V-11186-C
(974 lg)						0.37	0.48	0.85	
USA, (Wyoming), 1995	0.94 EC	0.27-0.28	2	70	seeds	0.63	0.46	1.1	V-11186-D
(Mycogen 452)						0.74	0.68	1.4	
USA, (Nebraska), 1995	0.94 EC	0.28	2	70	seeds	0.68	0.43	1.1	V-11186-E
(s 3446)						0.68	0.43	1.1	
USA, (Texas), 1995	0.94 EC	0.28	2	70	seeds	0.38	0.24	0.62	V-11186-F
(Mycogen 675)						0.38	0.26	0.64	
USA, (Missouri), 1995	0.94 EC	0.27-0.28	2	69	seeds	0.34	0.18	0.52	V-11186-G
(Sunbred 256)						0.31	0.15	0.46	
		0.54-0.57	2	69	seeds	0.55	0.25	0.80	
						0.74	0.26	1.0	
USA, (Nth Dakota), 1995	0.94 EC	0.27-0.28	2	72	seeds	2.5	1.2	3.7	V-11186-H
(Sicgo 458)						2.5	1.3	3.8	
		1.33-1.45[6]	2	72	seeds	12	5.9	18	
						14	7.8	22	
Canada, (Saskatoon),	240 EC	0.045	1	72	seeds	0.026	0.025	0.051	Cosgrove
1994, (Aurora)						<0.02	<0.02	<0.04	96-035 [7]
		0.09	1	72		0.80	0.12	0.2	
						0.067	0.063	0.13	
		0.180	1	72		0.08	0.10	0.18	
						0.079	0.085	0.16	
		0.045	1	86	seeds	<0.02	<0.02	<0.04	
						<0.02	<0.02	<0.04	
		0.09	1	86		<0.02	<0.02	<0.04	
						<0.02	<0.02	<0.04	
		0.180	1	86		<0.02	0.025	0.045	
						<0.02	<0.02	<0.04	
Canada, (Saskatoon),	240 EC	0.09	1	81	seeds	0.076	0.060	0.14	
1994, (Aurora)						0.054	0.071	0.13	
		0.18	1	81	seeds	0.16	0.28	0.44	
		0.09	1	96	seeds	0.058	0.061	0.12	
						0.048	0.037	0.085	
		0.18	1	96	seeds	0.11	0.05	0.16	

Country, year, (variety)	Application			PHI, days	Sample	DME	DME-OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
						0.066	0.053	0.12	
Canada, (Manitoba),	240 EC	0.09	1	88	seeds	<0.02	<0.02	<u>≤0.04</u>	Cosgrove
1995, (Dahlgren)						<0.02	<0.02	<0.04	96-035 [7]
		0.18	1	88	seeds	<0.02	<0.02	<0.04	
						<0.02	<0.02	<0.04	
Canada, (Manitoba),	240 EC	0.09	1	94	seeds	<0.02	<0.02	<u>≤0.04</u>	
1995, (Pioneer)						<0.02	<0.02	<0.04	
		0.18	1	94	seeds	<0.02	<0.02	<0.04	
						<0.02	<0.02	<0.04	
Canada, (Saskatoon),	240 EC	0.09	1	83	seeds	<0.02	<0.02	<u>≤0.04</u>	
1995, (Sierra)						<0.02	<0.02	<0.04	
		0.18	1	83	seeds	<0.02	<0.02	<0.04, <0.04	
France, (Mongauzy),		0.18	1	108	seeds	<0.03	<0.03	<u>≤0.06</u>	Tomen, 1988, TE 2286 [8]
1987, (Frankasol)									
France, (Veigne), 1987, (Viki)		0.48	1	111	seeds	<0.03	<0.03	<u>≤0.06</u>	TE 2287 [9]
France, (Esvres), 1987, (Mirasol)		0.48	1	123	seeds	<0.03	<0.03	<u>≤0.06</u>	TE 2288[10]
France, (Vacquiers),	240 EC	0.48	1	100	seeds			<u>≤0.03</u>	Tomen France, 1997, BKA/620/96 [11]
1996, (Albena)									
France, (Mas Thibert),	240 EC	0.48	1	101	seeds			<u>≤0.03</u>	BKA/620/96 [12]
1996, (Marko)									
France, (St Martin de Sanzay), 1997,	240 EC	0.52	1	100	seeds	0.07	0.06	<u>0.13</u>	Tomen France,
(Alladin)	2 EC	0.29	1	100	seeds	0.18	0.15	<u>0.33</u>	1998, F97017R [13]
France, (Sarrians), 1997,									
(Pistol)	240 EC	0.51	1	100	seeds	<0.03	<0.04	<u>≤0.07</u>	F97018R [14]
	2 EC	0.31	1	100	seeds	<0.03	<0.04	<u>≤0.07</u>	
	240 EC	0.24	1	74	seeds			<0.03	0292-89 [15]
Italy, (Romauldo), 1989,									
(Pharaon)				92				<0.03	
				110				<u>≤0.03</u>	
				110	oil			<u>≤0.03</u>	
Italy, (Ravenna), 1991,	240 EC	0.24	1	60	seeds	0.07	0.13	0.20	
(Pharron)				75		0.06	0.13	0.19	102660 [16]
				90		0.05	0.10	<u>0.15</u>	
Italy, (Latina), 1991,	240 EC	0.24	1	60	seeds	0.04	0.12	0.18	
(Montenuovo)				75		0.06	<0.03	<0.09	103403 [17]
				90		0.05	<0.03	<u>≤0.08</u>	

Country, year, (variety)	Application			PHI, days	Sample	DME	DME-OH	Total residues, mg/kg	Ref.
	Form.	kg ai/ha	No.						
GAP									
Argentina	**240 EC**	**0.16-0.24**		**100**					
Canada	**240 EC**	**0.045-0.09**	**1-2**	**72**					
Italy/France	**240 EC**	**0.18-0.48**		**100**					
Italy/France	**240 EC**	**0.18-0.48**		**100**					

[1] Applied at 8-leaf stage of growth. Limit of detection 0.05 mg/kg; recovery from seed at 0.1 mg/kg 81%.
[2]Applied at 10-leaf stage. Limit of detection 0.05 mg/kg; recovery at 0.1 mg/kg 55%.
[3]Limit of detection 0.05 mg/kg; recovery at 0.1 mg/kg of clethodim and 5-OH-clethodim sulfone 76% and 104% respectively from hulls, 92% and 128% from solvent-extracted presscake, 63% and 132% from expelled presscake, 85% and 91% from refined oil, 88% and 136% from seeds.
[4] Single application at flowering. Limit of detection 0.05 mg/kg; recovery of clethodim at 0.1 mg/kg 79% from seeds.
[5] Limit of detection 0.1 mg/kg; recovery from seed at 0.2, 0.5 and 1 mg/kg 82-118% of clethodim sulfoxide, 71-107% of 5-OH-clethodim sulfone.
[6] Processing study, with Select applied at fivefold rate. Seeds were processed into meal, crude oil and refined oil. Residues were 33 mg/kg in meal, 3.2 and 3.5 mg/kg in crude oil and <0.1 mg/kg in refined oil.
[7] Limit of detection 0.02 mg/kg; recovery of clethodim sulfoxide at 0.02, 0.1 and 0.2 mg/kg from seed 65-119% (n = 10).
[8] Limit of detection 0.03 mg/kg; recovery of clethodim at 0.06 and 0.1 mg/kg 72 and 82%.
[9] Limit of detection 0.03 mg/kg; recovery of clethodim at 0.06 and 0.1 mg/kg 100 and 104%.
[10] Limit of detection 0.03 mg/kg; recovery of clethodim at 0.06 and 0.1 mg/kg 95 and 65%.
[11] Single application 6-7 leaf stage. Limit of detection (total residues) 0.03 mg/kg; recovery at 0.03 mg/kg 87, 87 and 93%. Method RM 26B-2.
[12] Single application at 4 extended nodes stage of growth. Limit of detection 0.03 mg/kg; recovery at 0.03 mg/kg 87, 87 and 93%. Method RM 26B-2.
[13] Single application at appearance of flower buds. Limit of detection 0.07 mg/kg (total residues), 0.03 mg/kg DME and 0.04 mg/kg DME-OH; recovery of clethodim 64, 81 and 89% at 0.07 mg/kg, 85% at 0.7 mg/kg. Method RM-26B-2.
[14] Single application at 8-leaf stage. Limit of detection 0.07 mg/kg (total residues), 0.03 mg/kg DME and 0.04 mg/kg DME-OH; recovery of clethodim 64, 81 and 89% at 0.07 mg/kg, 85% at 0.7 mg/kg. Method RM-26B-2.
[15] Single application by spraying. Limit of detection 0.03 mg/kg; recovery of clethodim at 0.03 mg/kg 79%. Plot size 1300 m^2, silt soil, pH 8, 1% C.
[16] Single application at appearance of flowers. Plot size 90 m^2. Limit of detection 0.03 mg/kg DME and DME-OH; recovery 99, 112 and 116% at 0.03 mg/kg and 92 and 108% at 0.05 mg/kg.
[17] Single application at flower development. Plot size 200 m^2. Limit of detection 0.03 mg/kg DME and DME-OH; recovery 99, 112 and 116% at 0.03 mg/kg and 92 and 108% at 0.05 mg/kg.

Animal feeding studies

Feeding studies on laying hens and dairy cattle which had been reviewed in 1994 were re-submitted by the manufacturer. Both studies are discussed here in relation to the estimation of the dietary exposure of livestock of treated feed items.

Groups of laying hens were dosed orally by gelatin capsule with a mixture of clethodim and clethodim sulfoxide (Fletcher and Pedersen, 1988). Doses were prepared daily and administered on day 1 and every day thereafter for 28 days. Each group consisted of 20 hens which were dosed according to the following regime.

Group	Dose, ppm in the diet		Dose, mg/kg body weight*	
	Clethodim	Clethodim sulfoxide	Clethodim	Clethodim sulfoxide
T-1	0.5	9.5	0.04-0.09	0.80-1.79
T-2	1.5	28.5	0.13-0.28	2.39-5.39
T-3	5.0	95.0	0.42-0.95	7.98-17.96

* Based on a maximum feed level of 151.3 g/bird/day and body weight range of 800-1800 g/bird.

Eggs were collected on days -1, 1, 2, 4, 7, 14, 21, 28, 29 and 30 and pooled from sub-groups of 10 birds within each treatment group. On day 29, ten hens from each group were killed and samples of muscle (thigh and breast), liver, gizzard and fat (subcutaneous and abdominal) were collected for analysis. The remaining hens in each group were killed on day 31, two days after the end of dosing.

The method of analysis was the common moiety method RM-26A, described in PAM, Vol. II, Pesticide Registration Section 180.412, with minor modifications to the gas-chromatographic conditions. A full description of the method was provided in the analytical phase of the report (Lear, 1989). Recoveries of clethodim, 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide from fortified eggs, fat, gizzard, liver and muscle were reported. The reported limit of detection was 0.05 mg/kg for each compound in all samples. The results are shown in Table 28.

Table 28. Recoveries from fortified hen tissues and eggs in a feeding study (Lear, 1989).

Sample	Fortification level, mg/kg	Recovery, %		
		Clethodim	5-OH-clethodim sulfone	S-Me-clethodim sulfoxide
Eggs	0.1	57-96	56-94	66-95
	0.5	61-75	66-70	56-67
Fat	0.1	63-98	48-166	47-93
	0.5	73, 83	73, 81	67, 76
	1.0	71-72	63-67	62-64
Gizzard	0.1	70-110	61-88	61-93
	0.5	85	82	75
	1.0	87	71	75
Liver	0.1	67-126	70-113	63-94
	0.5	83, 93	82, 85	74, 82
	1.0	78, 87	76, 76	72, 82
Muscle	0.1	82-120	71-110	71-90
	0.5	83, 93	79, 84	72, 79
	1.0	55, 79	68, 74	54, 73

The residues found in the eggs are shown in Table 29.

Table 29. Total clethodim residues in eggs after dosing at three levels.

Day	Residues, mg/kg, in group								
	T-1			T-2			T-3		
	C	5-OH CSO2	S-Me CSO	C	5-OH CSO2	S-Me CSO	C	5-OH CSO2	S-Me CSO
1	<0.05	<0.05	<0.05	0.06	<0.05	<0.05	0.21	<0.05	<0.05
2	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.21	<0.05	<0.05
4	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.19	<0.05	<0.05
7	<0.05	<0.05	<0.05	0.07	<0.05	<0.05	0.15	<0.05	<0.05
14	<0.05	<0.05	<0.05	0.08	<0.05	<0.05	0.17	<0.05	<0.05
21	<0.05	<0.05	<0.05	0.09	<0.05	<0.05	0.14	<0.05	<0.05
28	<0.05	<0.05	<0.05	0.05	<0.05	<0.05	0.24	<0.05	<0.05
29	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
30	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05

C: clethodim
5-OH CSO_2: 5-OH-clethodim sulfone
S-Me CSO: *S*-methyl-clethodim sulfoxide

The residues of clethodim during dosing were <0.05-0.09 mg/kg in the T-2 group and 0.14-0.24 mg/kg in T-3. One day after withdrawal of dosing, clethodim residues were below the limit of detection. The sulfone and sulfoxide were below the limit of detection in all the samples.

Clethodim, *S*-methyl-clethodim sulfoxide and 5-OH-clethodim sulfone were not detected above 0.05 mg/kg in any fat, muscle or gizzard samples. The only residue above this level was in one day 29 sample of liver in group T-3 (5 ppm clethodim + 95 ppm clethodim sulfoxide) which contained 0.06 mg/kg of DME; 5-OH-clethodim sulfone and *S*-methyl-clethodim sulfoxide were not detected above 0.05 mg/kg in any liver samples.

The results show that clethodim and clethodim sulfoxide do not accumulate in hen tissues.

Dairy cattle were dosed orally by capsule for 28 days with a mixture of clethodim and clethodim sulfoxide (Weissenburger *et al.*, 1989). Groups of four cows were treated according to the following regime.

Group	Dose equivalent, ppm in the diet		Dose, mg/kg body weight*	
	Clethodim	Clethodim sulfoxide	Clethodim	Clethodim sulfoxide
T-1	0.5	9.5	0.015-0.017	0.28-0.32
T-2	1.5	28.5	0.044-0.046	0.83-0.88
T-3	5.0	95.0	0.13	2.48-2.60

* Based on a maximum feed level of 17.65 kg/cow and body weight ranges of 518-594 kg (T-1); 566-603 kg (T-2); 644-676 kg (T-3).

Three cows from each group were slaughtered on day 29 (22-24 hours after the last dose) and samples of muscle, fat (peritoneal and subcutaneous), liver and kidney were taken for analysis.

The animals were milked in the morning and evening and the milk from each treatment group was composited for analysis. Milk samples taken on days 1, 2, 4, 7, 12, 16, 20, 24, 28, 29, 30 and 31 were analysed, those from days 29, 30 and 31 being from a cow which had been withdrawn from dosing for 1, 2 and 3 days. Milk samples from the T-3 group on days 25, 26 and 27 were composited for processing into skimmed milk, cream and acid whey for comparison of the residues in the processed commodities with the levels in whole pasteurised milk.

The residues were quantified as S-methyl-DME, DME or DME-OH and reported as clethodim (Weissenburger and Krupiak, 1988a,b). Recoveries from milk were determined by fortification with clethodim, *S*-methyl-clethodim sulfoxide and 5-OH-clethodim sulfone at 0.0125, 0.025, 0.05 and 0.1 mg/kg. Tissues were fortified with 0.05 and 0.1 mg/kg. The limits of determination were reported as 0.0125 mg/kg in milk and 0.05 mg/kg in liver, kidney, muscle and fat.

The maximum residues found in milk, processed milk products and tissues are shown in Tables 30, 31 and 32.

Table 30. Maximum residues in milk of cows dosed at three levels.

Group	Maximum residues, expressed as mg/kg clethodim		
	DME	S-methyl DME	DME-OH
T-1	<0.0125	<0.0125	<0.0125
T-2	0.0334	<0.0125	<0.0125
T-3	0.0812	0.0316	<0.0125

Table 31. Total clethodim residues in processed milk products from cows dosed at the equivalent of 100 ppm in the diet (T-3).

Commodity	Maximum residues expressed as mg/kg clethodim		
	DME	S-methyl DME	DME-OH
Pasteurised whole milk	0.0606	0.0139	<0.0125

Skimmed milk	0.0269	<0.0125	<0.0125
Cream*	0.1096	<0.0125	<0.0125
Acid whey	0.0265	<0.0125	<0.0125

*Butterfat content ranged from 2.8 to 4.5% in the whole milk.

Table 32. Maximum clethodim residues in cattle tissues.

Group	Sample	Residues expressed as mg/kg clethodim		
		DME	S-methyl DME	DME-OH
T-1	Liver	0.059	<0.05	<0.05
	Kidney	0.051	<0.05	<0.05
	Muscle	<0.05	<0.05	<0.05
	Fat	<0.05	<0.05	<0.05
T-2	Liver	0.119	<0.05	<0.05
	Kidney	0.170	<0.05	<0.05
	Muscle	<0.05	<0.05	<0.05
	Fat	0.052	<0.05	<0.05
T-3	Liver	0.445	0.087	<0.05
	Kidney	0.538	0.078	<0.05
	Muscle	0.070	<0.05	<0.05
	Fat	0.153	<0.05	<0.05

Recoveries from tissues and milk are shown in Table 33.

Table 33. Recoveries from fortified cattle tissues, milk, and processed milk products.

Sample	Fortification level, mg/kg	Recovery, %		
		Clethodim	*S*-methyl-clethodim sulfoxide	5-OH-clethodim sulfone
Liver	0.05	79	91	78
	0.1	72	80	78
Kidney	0.05	83, 86	100, 100	90, 109
	0.1	77	78	89
Muscle	0.05	79	91	96
	0.10	88	86	104
Fat	0.05	86	90	85
	0.10	70	71	76
Whole milk	0.10	87	95	106
Cream	0.10	70	78	94
Skimmed milk	0.05	80	80	105
Acid whey	0.05	71	80	74
Milk	0.0125	103, 106	95	96, 115
	0.025	78, 96	67, 97	65, 110
	0.05	78, 80, 82, 85, 85, 87, 98	80, 83, 103, 77	70, 80, 84, 86, 86, 91, 93
	0.10	70, 72, 73, 75, 79, 80, 83, 85, 92, 99	74, 78, 83, 85, 86, 88, 96	72, 73, 74, 83, 87, 94, 96, 97, 98, 109

The residues in the tissues of animals slaughtered 2 days after the withdrawal of dosing were <0.05 mg/kg in all groups. Similarly, the levels of each component of the residue in the milk after withdrawal of dosing for 1, 2 and 3 days were <0.0125 mg/kg.

Estimation of dietary burden of livestock

Estimates of the exposure of cattle and hens to clethodim residues in treated feed items are shown in Tables 35 and 36. Maximum and median residues in animal feed commodities are shown for comparison. All median residues have been estimated from the results of trials which were considered to conform to GAP. Data from the 1994 and 1997 monographs have been included where relevant and processing factors derived where possible. Where the dry matter content is 85% or higher no

adjustment for moisture has been made. Items for which intake figures were not available have been included as they may be used in animal feed.

An intake of 15 kg dry matter/day was assumed for cattle, with an average body weight of 500 kg.

Table 34. Estimated dietary intake of clethodim residues from treated feed by cattle. The items contributing mainly to the intake are shown bold.

Crop or Commodity		Maximum residue, mg/kg	Median residue, mg/kg	Maximum % in diet	% DM	Intake, mg/animal/day	Reference
Alfalfa	**hay**	8.9	1.6	**70**		**16.80**	JMPR 1997 [1]
Bean	hay	5.5	1.8	25 [2]	88	6.75	Table 26
	vines	2.8 (dry wt)	1.5 (dry wt)	25 [2]	25	5.62	
Clover	forage	0.07		30	30	1.03	JMPR 1997
Cotton	seed	0.48	0.15	25	88	0.56	JMPR 1994
	hulls		0.18	20		0.54	
	meal		0.25	15		0.56	
Field peas		2.0	0.08	20	90	0.24	JMPR 1997
Fodder beet		<0.03	0.03	20 [3]		0.09	JMPR 1997
Lupins			<0.1	20	88	0.3	JMPR 1997
Pea straw			<0.1	25	88	0.38	JMPR 1997
Peanut	vines	12	1.13	25	85	4.23	
	hay	2.6	0.57	25		2.13	
	meal		3.1	**15**	85	**6.97**	JMPR 1997
Rape seed meal		1.5		**15**	88	**3.37**	JMPR 1994
Soya bean meal		10		**15**	92	**22.50**	JMPR 1994
Sugar beet tops			<0.03	20	23	0.39	JMPR 1997
Sunflower meal		1.4	0.38	15	92	0.85	Tables47 28,
Tomato pomace			1.2	10		1.80	JMPR 1997

[1]Residue evaluation, Table 35
[2] Taken from OPPTS 860.1000 (USEPA)
[3] Figure for sugar beet used

The highest contributions come from soya bean meal, alfalfa hay, peanut meal and rape seed (canola) meal. The total exposure is calculated to be 46.3 mg clethodim/animal/day or 3.1 ppm in the diet from a diet of alfalfa hay, soya bean meal and peanut meal. The lowest dose in the cow feeding study was equivalent to 10 ppm clethodim (0.5 mg/kg clethodim and 9.5 mg/kg clethodim sulfoxide). At this dose level, each component of the residue in the whole milk, muscle and fat was below the limit of determination. In the milk the total residues were equivalent to <0.0375 mg/kg and in muscle and fat to <0.15 mg/kg. Residues of 0.059 and 0.051 mg/kg DME were found in liver and kidney respectively, with corresponding total residues of <0.16 and <0.151 mg/kg.

Hens were assumed to have a body weight of 2 kg and a feed intake of 150 g dry matter/day. The estimated intake of clethodim residues is shown in Table 35.

Table 35. Estimated dietary intake of clethodim residues from treated feed by hens. The items contributing mainly to the intake are shown bold.

Commodity	Maximum residue, mg/kg	Median residue, mg/kg	Maximum % in feed	% DM	Intake, mg/hen/day
Cotton meal		0.25	20	89	0.0075
Field peas		0.08	20	90	0.0024
Lupins		<0.01	15	88	0.0003
Peanut meal		3.1	25	85	**0.1163**
Rape seed meal	1.5		15	88	**0.0338**
Soya beans	10		20	89	**0.3**

Commodity	Maximum residue, mg/kg	Median residue, mg/kg	Maximum % in feed	% DM	Intake, mg/hen/day
Soya bean meal	10		40	92	**0.6**
Sunflower meal		0.38	30	92	0.017

The highest possible exposure in the hen diet is calculated to be 1.05 mg/bird/day or 7 ppm in a diet composed of peanut meal, rape seed meal, soya beans and soya bean meal. The lowest dose in the hen feeding study was equivalent to 10 ppm clethodim (0.5 mg/kg clethodim and 9.5 mg/kg clethodim sulfoxide). At that level each component of the residue in all tissues and eggs was <0.05 mg/kg and the total clethodim residues <0.15 mg/kg.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were available.

In processing

Processing studies on oilseed crops (cotton seed, canola, peanuts, soya beans and sunflowers), tomatoes and sugar beet were reported. The stability of residues in processed fractions of peanuts and tomatoes was discussed in the section on methods of residue analysis.

Canola. Crops at two sites in Canada were treated with Select 240 EC herbicide at about twice the maximum label rate (Cosgrove, 1990a,b). The single application was made at the 2-3 leaf stage of growth and the crops were harvested 67 and 75 days after treatment. The residues in the seed are shown in Table 36 and details of the trials are given as footnotes. The seed from the Saskatchewan trials was processed into meal, crude oil, hydrogenated oil, deodorised hydrogenated oil and deodorised oil. Residues in crude oil and desolventized meal were reported (Table 37).

Table 36. Residues in canola seed from an exaggerated treatment with clethodim in Canada, 1989.

Location, (variety)	Application			PHI, days	Residues, mg/kg			Reference
	Form.	kg ai/ha	No.		DME	DME-OH	Total	
Manitoba	240 EC	0.24	1	75	0.078	0.119	0.197	Cosgrove 1990[1]
(Tobin)					0.065	0.122	0.187	
Saskatchewan	240 EC	0.21	1	66	0.077	0.205	0.282	Cosgrove 1990[2]
(Westar)					0.099	0.230	0.329	
					0.067	0.224	0.291	

[1] Single application with 1%v/v corn oil using tractor-mounted pump. Plot size 1 ha, sandy loam soil.
[2] Single application with 1 % corn oil using tractor-mounted pump. Plot size 1 ha, silty clay soil.

Table 37. Residues in canola and its processed commodities, with processing factors.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Canola seed	0.081 (average)	0.220 (average)	0.301 (average)	-
Crude oil	<0.05	<0.05	<0.1	<0.3
Meal # 1	0.242	0.051	0.29	0.96
# 2	0.106	0.66	0.766	2.54

The meal samples were re-analysed and the second analysis (meal #2) showed total residues of 0.77 mg/kg in the meal, giving a concentration factor of 2.54. As residues above the limit of determination were not found in the crude oil, the remaining oil samples were not analysed. Recoveries were checked by fortification with clethodim sulfoxide and 5-OH-clethodim sulfone at

0.05 and 2 mg/kg. Recoveries of clethodim sulfoxide at 0.05 and 0.2 mg/kg were 76 and 86% in crude oil and 127 and 131% in meal; the corresponding recoveries of 5-OH-clethodim sulfone were 78 and 95% in crude oil and 125 and 98% in meal.

Cotton. Select 2 EC was applied to cotton at 8 times the maximum recommended seasonal rate in Mississippi (Lai, 1988a). The crop was treated with two applications (30-day interval) at a rate equivalent to 2.24 kg ai/ha, and harvested 40 days after the last application. The seed was processed into meal, hulls, crude oil, refined oil, soapstock, delinted seed, linters and linter motes (Table 38).

Table 38. Residues in cotton seed and its processed commodities from 2 x 2.24 kg ai/ha of 2 EC[1]. USA, 1987 (Lai, 1998a).

Location (variety)	Application			PHI, days	Sample	Residues, mg/kg			Processing factor
	Form.	kg ai/ha	No.			DME	DME-OH	Total	
Mississippi	2 EC	2.24	2	40	fuzzy seed	0.58	<0.1	<0.68	-
(DPL 41)						0.65	0.30	0.95	
						0.60	0.18	0.78	
					mean	0.61	0.19	0.80	
					meal	0.94	0.41	1.35	1.69
					hulls	0.78	<0.2	<0.98	1.22
					crude oil	0.14	<0.04	<0.18	0.22
					refined oil	<0.04	<0.04	<0.08	0.1
					soapstock	0.65	<0.2	<0.85	1.06
					delinted seed	0.67	0.21	0.88	1.1

[1] Applied by tractor-mounted sprayer with 1 qt/acre crop oil; plot size 4 rows of 61 m. Cotton stored for 24 hours before ginning, then frozen.

Recoveries were determined by fortification with clethodim sulfoxide and 5-OH-clethodim sulfone at 0.2, 0.5 or 1 mg/kg. Methods RM-26A and RM-26A-1 were used. The results are shown in Table 39.

Table 39. Recoveries from fortified cotton seed and processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO_2	CSO	5-OH CSO_2
Fuzzy seed	0.5	0.5	77, 82, 91	90, 109, 110
Meal	1.0	1.0	86	86
Hulls	1.0	1.0	85	78
Crude oil	0.2	0.2	77	57
Refined oil	0.2	0.2	75	57
Soapstock	1.0	1.0	82	56
Delinted seed	0.5	0.5	90	64

All recoveries of clethodim sulfoxide were acceptable. Recoveries of the sulfone were low from crude and refined oils, soapstock, and delinted seed.

Peanuts were treated twice with Select 2 EC at a rate equivalent to 1.4 kg ai/ha, 5 times the maximum recommended US rate, with a 14-day interval at the 'pegging' stage of crop growth (Lai, 1994b). The peanuts were harvested 40 days after treatment with an additional 3 days allowed for drying. The results and processing factors are shown in Table 40.

Table 40. Residues in peanuts and their processed commodities.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Kernels	3.6	0.32	3.9	-

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
	3.6	0.39	4.0 (average 4.0)	-
Meal	9.2	0.42	9.6	2.4
Crude oil	1.7	<0.04	1.7	0.4
Refined oil	0.32	<0.04	0.36	0.09
Soapstock	10	0.13	10.1	2.5

The results show a concentration of residues in peanut meal and soapstock. Analytical recoveries from the individual processed fractions are shown in Table 15.

Soya beans were treated twice with post emergent applications of Select 2 EC at 2.2 kg ai/ha (27 day re-treatment), equivalent to 8 times the maximum recommended US rate, and harvested after 40 days (Lai, 1988b). The beans were separated from the hulls and processed into meal, crude oil, refined oil, soapstock, degummed oil and crude lecithin. The residues are shown in Table 41.

Table 41. Residues in soya beans and their processed commodities.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Dry shelled bean	18, 21	8.7, 9.0	27. 30 (average 28.5)	-
Meal	22	5.2	27	0.95
Hulls	17	9.1	26	0.91
Crude oil	2.6	0.17	2.8	0.1
Refined oil	<0.04	<0.04	<0.08	<0.003
Soapstock	32, 32	1.3, 1.6	33, 34	1.2
Degummed oil	1.5	0.1	1.6	0.06
Crude lecithin	36	6.1	42	1.5

There was a slight concentration of clethodim residues in soapstock and crude lecithin. Recoveries were measured at 0.2 and 1 mg/kg by Methods RM-26A and RM-26A-1 (Table 43).

Table 42. Recoveries from fortified soya beans and processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO_2	CSO	5-OH CSO_2
Soya beans	1.0	1.0	88	102
Meal	1.0	1.0	76	64
Hulls	1.0	1.0	89	113
Crude oil	0.2	0.2	73	73
Refined oil	0.2	0.2	70	55
Soapstock	1.0	1.0	80, 85	90,, 120
Degummed oil	0.1	0.1	82	90
Crude lecithin	1.0	1.0	82	99

Sugar beets were treated at the fivefold rate of 1.4 kg ai/ha at the 5th and 12th leaf stages of growth (Lai, 1991) with an interval of 16 days between applications. The crops were harvested 99 days after treatment. The individual residues in the roots were below the limit of determination of 0.1 mg/kg (total <0.2 mg/kg). The roots were processed into sliced beets, dehydrated pulp, refined sugar and molasses. The residues are shown in Table 43.

Table 43. Residues in sugar beets and their processed commodities.

Sample	Residues, mg/kg		
	DME	DME-OH	Total
Sugar beets	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2
Sliced beets	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2

Sample	Residues, mg/kg		
	DME	DME-OH	Total
Dehydrated pulp	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2
Refined sugar	<0.1, <0.1	<0.1, <0.1	<0.2, <0.2
Molasses	0.24	<0.1	0.24

The results show a concentration in molasses, but processing factors could not be calculated as the residues in the raw beets were below the level of determination. Recoveries are shown in Table 44.

Table 44. Recoveries from fortified sugar beet and processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO_2	CSO	5-OH CSO_2
Sliced beets	0.2	0.2	74	76
Dehydrated pulp	0.2	0.2	83	72
Molasses	0.2	0.2	68	102
	0.5	0.5	74	100
Refined sugar	0.1	0.1	96	118
	0.2	0.2	63	64
	0.5	0.5	79	78

Sunflowers were treated twice at an interval of 15 days at 1.33-1.45 kg ai/ha, about 5 times the maximum recommended rate, with the last application at 50% flowering and harvested after 72 days (Lai, 1996c). The seed was processed into meal and crude and refined oil. The residues and processing factors are shown in Table 45.

Table 45. Residues in sunflower seeds and their processed commodities.

Sample	Residues, mg/kg			Processing factor
	DME	DME-OH	Total	
Seeds	10, 12	4.3, 5.9	14, 18 (average 16)	-
Hulls	16, 12	7.6, 5.8	18, 24 (average 21)	1.3
Meal	23, 23	10, 9.9	33, 33	2
Crude oil	2.8, 3.1	0.38, 0.40	3.2, 3.5 (average 3.3)	0.2
Refined oil	<0.1, <0.1	<0.1, <0.1	<0.1, <0.1	<0.006

There was some concentration of residues in the meal and hulls. Recoveries of clethodim sulfoxide and 5-OH-clethodim sulfone were determined at concentrations of 0.2, 0.5, 2.5 or 5 mg/kg with the results shown in Table 46.

Table 46. Recoveries from fortified sunflower seeds and their processed commodities.

Sample	Fortification level, mg/kg		Recovery, %	
	CSO	5-OH CSO_2	CSO	5-OH CSO_2
Seeds	5	5	94	89
Hulls	0.5	0.5	84	120
Meal	0.5	0.5	120	113
Crude oil	2.5	2.5	67	69
Refined oil	0.2	0.2	65	73

Tomatoes were treated twice with Select 0.94 EC at 1.4 kg ai/ha or 5 times the maximum recommended rate (Lai, 1995b). The applications were made at blooming or fruit set and immature fruit stages at an interval of 16 days. Fruit were harvested 20 days after the last application and processed into wet pomace, dry pomace, paste and juice. Two studies were conducted in consecutive years, with the results shown in Table 47.

Table 47. Residues in tomatoes and their processed commodities.

Sample	Total residues, mg/kg		Processing factor
	1993	1994	
Fruit	0.84	1.2	
Wet pomace	0.79	1.0	0.94, 0.83
Dry pomace	2.6	4.0	3.1, 3.3
Purée	–	2.6	2.2
Paste	2.9	3.6	3.5, 3.0
Juice	0.76	0.92	0.90, 0.77

There was a concentration of clethodim residues in purée, paste and dry pomace. Recoveries from juice, paste and pomace were within acceptable limits and are given in Tables 18 and 19.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided.

NATIONAL MAXIMUM RESIDUE LIMITS

The information provided is given below. The residue is considered to be defined as "sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulphoxides and sulfones, expressed as clethodim", unless otherwise stated.

Country	MRL, mg/kg	Commodity
Argentina	0.5	Cotton seed, peanut, soya bean, sunflower seed
	3.0	Soya bean straw, sunflower straw
	10	Alfalfa forage
	15	Alfalfa hay
Australia [1]	0.01*	Fennel (bulb)
	0.05*	Edible offal (mammalian), eggs, meat (mammalian), milk, poultry offal, poultry meat,
	0.05	Endive
	0.1*	Beans (except broad beans and soya beans), broad beans, cucurbits, peas, pulses (except lupins), spinach, sunflower seed
	0.1	Celery, lettuce (leaf and head), strawberry. tomato
	0.2	Flowerhead brassicas, cotton seed, lupins, poppy seed,
	0.3	Garlic, onion (bulb), leeks (T)
	1	Asparagus, root and tuber vegetables
	2	Peanut, peanut oil
Belgium	0.05	Fodder beet, onions, sugar beet
	0.1	Beans, peas, potatoes
Brazil	0.05	Garlic, onion, tomato, dry beans, potato, carrot, cotton seed
	1.0	Soya beans
Canada	0.1	Canola, seedling alfalfa, sunflower (including sunola)
	0.3	Flax
	0.4	Mustard seed
	0.5	Field peas, lentils, potatoes, desi and kabuli chickpeas
Czech Republic	0.03	Fodder beet (root and leaves), horse bean, oil seed rape, sugar beet (root and leaves)
	0.1	Potato
	0.3	Peas
France	0.05	Sugar beet
	0.1	Proteaginous peas, sunflower
Hungary	0.1	Forestry, mustard, potato, soya bean, sugar beet, sunflower, tomato
	0.2	Peas
Italy	0.2	Sugar beet, fodder beet, tomato
	1	Soya bean
Japan	0.1	Carrot, sweet potato, onion
	0.2	Sugar beet, kidney bean
	0.3	Azuki

Country	MRL, mg/kg	Commodity
Mexico	10	Soya bean
New Zealand	<0.1	White clover, seed crops, peas, lentils, oil seed rape, orchards, vegetables
Peru	1	Alfalfa
	5	Orange, apple, cotton seed
	10	Bean
Russia	0.1	Carrot, sugar beet, fodder beet, red beet, onion, soya bean, flax seed, flax
	0.2	Potato
Spain	0.05	Sunflower, onion, garlic, potato
	0.1	Beans, field peas, tomato, flaxseed
	0.3	Soya bean
Switzerland	0.05	Sugar beet, fodder beet
	0.1	Potato, vegetables
Ukraine	0.1	Carrot, sugar beet, fodder beet, red beet, onion, soya bean, flax seed
	0.2	Potato
USA	0.05	Milk
	0.2	Dry onions, garlic, shallots, sugar beet (roots), cattle fat, cattle meat, cattle meat by-products, eggs, goat fat, goat meat, goat meat by-products, hog fat, hog meat, hog meat by-products, horse fat, horse meat, horse by-products, poultry fat, poultry meat, poultry meat by-products, sheep fat, sheep meat, sheep by-products
	0.5	Potato, sugar beet (tops)
	1.0	Cotton seed, tomato
	2.0	Cotton seed meal, sugar beet (molasses), dry beans, tomato (purée)
	3.0	Peanut (nutmeat), peanut hay, tomato (paste)
	5.0	Peanut meal
	6.0	Alfalfa (forage)
	10	Soya bean, alfalfa (hay)
Uzbekistan	0.1	Onion, carrot, soya bean, beet
	0.2	Potato

[1] Listed with sethoxydim.

APPRAISAL

Clethodim was evaluated by the JMPR in 1994 and 1997. In the first evaluation MRLs were recommended for several crops and animal feed commodities. At the 1996 CCPR (28th Session), several matters were referred to the JMPR for further consideration. These included the characterization and quantification of metabolites in plant metabolism studies and a lactating goat study, methods of analysis for clethodim and sethoxydim, and the lowest reported limit of determination in animal commodities.

In the 1997 evaluation some of the above issues were discussed, including a compound-specific method which allowed residues arising from the use of clethodim to be distinguished from those from sethoxydim. Additional studies on alfalfa, artichokes, cabbage, field peas, lupins, carrots, cauliflower, clover, celery, flax, garlic, cucumbers, leeks, lentils, lettuce, onions, peaches, peppers, spinach, summer squash (zucchini) and tomatoes were reviewed. MRLs for beans, sunflower seed and sunflower seed oil (crude and edible) were recommended for withdrawal.

At the 1999 CCPR, comments were made in relation to the MRLs recommended for cattle meat and cattle offal and the corresponding limits of determination for the two commodities. Moreover, it was noted that no justification was provided for the animal commodity MRLs on the basis of the levels of clethodim found in treated feed items. It was suggested that the JMPR should provide an estimate of the exposure of livestock through the feeding of treated commodities.

For the present evaluation, new trials on cucumbers, dry beans, peppers and sunflowers were reported, together with processing data for canola (rape seed), cotton seed, peanuts, soya beans, sugar beet, sunflowers and tomatoes. Data from previously reviewed Canadian trials on potatoes were also submitted with new data to allow a review of the MRL for potato. Data on photodegradation,

adsorption and fate in water/sediment systems were also submitted for evaluation. In order to respond to some of the issues raised by the CCPR, some metabolism and feeding studies reviewed in 1994 and 1997 were re-examined.

The predominant metabolites formed by the biochemical transformation of clethodim in hens and goats are clethodim sulfoxide, clethodim sulfone and *S*-methyl-clethodim sulfoxide. In plants, the main metabolites are clethodim sulfoxide and imine sulfoxide. In the metabolism studies, a comparison between the method used to determine the total radioactivity and a non-specific enforcement method in goat liver and kidney, hen muscle and soya beans was reported. The comparison shows that total residues determined by the routine methods of enforcement are very similar to the total radioactive residues found in the tissues and soya beans, and confirms that the residue definition for routine enforcement is appropriate. The routine method is not compound-specific however, and does not differentiate between residues originating from the use of clethodim and those arising from the use of sethoxydim.

The rates of degradation of clethodim, clethodim sulfoxide and clethodim sulfone were investigated in sterile and non-sterile soils. The calculated half-lives for the degradation of all the compounds were higher in sterile than in non-sterile soils, indicating that degradation is a function of microbial activity as well as temperature.

The adsorption and desorption of clethodim, clethodim sulfoxide and clethodim sulfone in five different soils were investigated. The results showed that all three compounds are weakly adsorbed to the soils tested, with K_d values ranging from <0.2 to 1.6.

Clethodim is degraded rapidly by photolysis in water in the presence of a photosensitiser such as acetone. Calculated half-lives were 0.94, 1.22 and 0.52 days, respectively, in solutions at pH 5, 7 and 9 which were exposed to natural sunlight for up to 30 days. Photolytic mechanisms of transformation include oxidation at the thioethyl function, elimination of the chloroallyl side chain to form clethodim imine and clethodim oxazole, and further oxidation to the oxazole sulfoxide and the sulfide and sulfoxide of dimethyl 3-[2-(ethylsulfonyl)propyl]pentanedioate (DME).

The hydrolysis of clethodim was investigated in sterile water at pH 5, 7 and 9 in the dark. HPLC analysis of the solutions at intervals up to 32 days showed that at pH 5 and 7, clethodim was an equilibrium mixture of two oxime forms, *anti* and *syn* conformations caused by H-bond formation between the oxyimino oxygen and the hydroxyl group on the hydroxy-cyclohexenone ring. Interconverison was fastest at pH 5. The resulting degradation products included an oxazole and a hydroxyvinyl compound.

In response to questions raised by the CCPR regarding a compound-specific method of analysis, new validation experiments were reported with milk, eggs and hen liver. A limit of 0.02 mg/kg was reported for clethodim, clethodim sulfoxide and *S*-methyl-clethodim sulfoxide in milk. In the goat metabolism study, the radioactivity in milk was predominantly due to clethodim sulfoxide, *S*-methyl-clethodim sulfoxide and lactose derivatives at levels of 20%, 5.5% and 30-50% respectively, so the method has been validated and recoveries determined with the appropriate metabolites. The limit of determination of total residues in milk was <0.04 mg/kg.

In tissues, the limit of determination was reported as 0.2 mg/kg with recoveries of clethodim sulfoxide at that level reported for hen tissues, beef liver and beef muscle. Results from the hen and goat metabolism studies showed that clethodim sulfoxide and *S*-methyl sulfoxide were the predominant sources of the radioactivity in tissues. The compound-specific method has therefore been validated for one of the main metabolites, with acceptable recoveries reported in hen and cattle tissues. The limit of determination for total residues by the non-specific common moiety method would be 0.04 mg/kg in tissues or thereabouts. This is comparable to the limit of determination found in the cow and hen feeding studies, where the common moiety method was employed.

In eggs, the compound-specific method was validated at 0.05 mg/kg and recoveries were determined at this level with clethodim sulfoxide. In the hen metabolism study, clethodim sulfoxide was the main source of the radioactivity in egg white and egg yolk during the 5-day dosing period. The method is therefore capable of quantifying clethodim residues in eggs down to a limit of 0.05 mg/kg.

Specialised methods were reported for soil and water where total clethodim residues included clethodim sulfoxide, clethodim sulfone, and the oxazole sulfoxide and oxazole sulfone. These compounds were characterized in studies of degradation in soil and water.

Studies of the storage stability of clethodim residues in alfalfa (forage and hay), celery, clover, cotton seed, beans (seeds, vines and hay), onions, peanuts and their processed commodities, sugar beet (tops and roots), sunflower seeds, tomatoes and their processed commodities, chicken tissues and eggs, and bovine tissues and milk were reported. In all the studies, clethodim residues were adequately stable during the period of storage. Discernible losses (≤20%) occurred in peanut soapstock at 429 days and in tomato paste and juice after 153-162 days. Freshly fortified samples were analysed concurrently with the stored samples. The Meeting agreed that <20% decrease in stored samples did not constitute degradation.

Residue data were submitted for cucumbers, dry beans, peppers (sweet and chilli), potatoes and sunflowers. Registered use patterns were reported only for these crops; further information on GAP is reported in the 1994 and 1997 monographs.

Data on residues in potatoes were submitted in response to questions raised at the 1999 CCPR on the registered use pattern in Canada and the establishment of an import tolerance in the USA. In the 1994 evaluation, data from France, Italy and the Ukraine were reviewed and an MRL of 0.2 mg/kg was recommended. The new data from Canada show that residues above 0.2 mg/kg were found in potatoes treated in accordance with Canadian GAP (single application at 0.09 kg ai/ha and a PHI of 60 days). The residues in the tubers were <0.1-0.46 mg/kg at PHIs of 45 or 46 days and <0.1-0.34 mg/kg at PHIs of 59 or 60 days. The residues in rank order were <0.1 (15), 0.137, 0.141, 0.19, 0.232, 0.326, 0.339, 0.348 and 0.463 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg. An STMR could not be estimated as the previously reviewed data from France, Italy and the Ukraine were not re-submitted.

Data on cucumbers were reported from trials in the USA and a trial in Poland. The trials in the USA are indicated as being in accordance with GAP, but the use pattern is not yet registered with the USEPA. The Meeting did not estimate a maximum residue level or an STMR as the registration was only pending.

Residue data on dry beans were generated in Brazil and the USA. In the 1994 evaluation data from Brazil only were the basis of the recommended MRL of 0.1 mg/kg. In 1997 an STMR of 0.05 mg/kg was estimated. The manufacturer resubmitted data previously reviewed in 1994 and 1997. The registered use pattern in Brazil allows application of clethodim at rates of 0.084-0.11 kg ai/ha with a PHI of 40 days. The registered use pattern in the USA allows 1 or 2 applications at rates equivalent to 0.11-0.28 kg ai/ha and a PHI of 30 days. The new data from the USA include residues in the whole seeds, hay and dry vines. The residues in the dry beans in rank order were <0.1, <0.5, 0.64, 0.79, 0.81, 0.98, 1.1, 1.41 and 1.6 mg/kg. On the basis of the combined Brazilian and US data, the Meeting recommended an MRL of 2 mg/kg and estimated an STMR of 0.81 mg/kg for dry beans. The 1997 Meeting recommended the withdrawal of the draft MRL of 0.1 mg/kg.

The residues in bean hay in rank order were <0.1, 1.3, 1.4, 1.5, 1.8, 2.0, 2.3, 3.3 and 5.5 mg/kg. The Meeting recommended an MRL of 10 mg/kg for bean fodder (hay) and estimated an

STMR of 1.8 mg/kg for animal feed purposes. The residues were not corrected for dry matter content (88%).

The residues in dry bean vines in rank order were <0.1, 0.23, 1.2, 1.5 (2), 1.8 (2), 2.2 and 2.8 mg/kg. The Meeting recommended an MRL of 5 mg/kg for bean forage and estimated an STMR of 1.5 mg/kg for animal feed purposes. As the residues in vines were expressed on a dry weight basis, a correction for dry matter content is not required for the calculation of the dietary burden for livestock.

Supervised residues trials on peppers were conducted in Italy and the USA. No registered use pattern or label was provided from Italy so the data could not be compared to relevant GAP. In the USA the registration of clethodim for use on peppers is pending. The proposed GAP is given as 1 or 2 applications at rates of 0.14-0.28 kg ai/ha with a PHI of 20 days. The residues in bell peppers (capsicums) and chilli peppers in trials which corresponded with the proposed GAP were 0.11-0.89 mg/kg. As the registration for peppers is pending, the Meeting did not estimate a maximum residue level or STMR.

Trials on sunflowers were carried out in Argentina, Canada, France, Italy and the USA. The Argentinian data were reviewed in 1994 and an MRL of 0.2 mg/kg was recommended. In the following review in 1997, the recommendation was withdrawn as there were too few results from trials according to GAP. The registered use pattern in Argentina allows single applications at rates of 0.16-0.24 kg ai/ha and a PHI of 100 days. GAP in Canada allows 1 or 2 applications at rates of 0.045-0.09 kg ai/ha with a PHI of 72 days and in France rates of 0.18-0.48 kg ai/ha with a PHI of 100 days. As a label from Italy was not provided, the Italian data were evaluated against French GAP. In the USA there is a pending use pattern of 0.11-0.28 kg ai/ha and a PHI of 70 days; the number of applications is not specified. As the registration is pending the US data were not used in the estimation of the STMR or maximum residue level. The residues in sunflower seed in rank order were <0.03 (3), <0.04 (5), <0.05, 0.051, <0.06 (3), 0.065, <0.07 (2), <0.08, 0.085, 0.12, 0.13 (2), 0.14, 0.15, 0.16, 0.20 and 0.33 mg/kg. The Meeting recommended an MRL of 0.5 mg/kg and estimated an STMR of 0.06 mg/kg. The draft MRL of 0.2 mg/kg was recommended for withdrawal by the 1997 JMPR.

A processing factor of 0.2 for crude sunflower seed oil was derived from a processing study on sunflowers. This processing factor may be applied to the recommended MRL to estimate a maximum residue level for crude sunflower seed oil. The STMR is calculated as 0.012 mg/kg for intake estimation. In the 1997 evaluation the draft MRLs for crude and edible sunflower seed oil were recommended for withdrawal owing to insufficient data. The Meeting recommended an MRL of 0.1* mg/kg for crude sunflower seed oil.

Feeding studies with laying hens and dairy cattle were reviewed in 1994 and 1997. The studies are repeated here for completeness. Doses in both studies were composed of a mixture of clethodim and clethodim sulfoxide (5:95), to simulate the exposure that may occur from feeding treated crops and processed commodities. At the 1999 CCPR, the JMPR was requested to justify the recommended MRLs for animal commodities by estimating the dietary exposure to livestock from feeding treated crops. Tables listing various treated feed commodity items and the residues likely to be found in them were constructed for a hen and dairy cow diet, and estimates of the composition of the diets were based on figures given in the FAO Manual and listed in USEPA guideline OPPTS 860.1000. Estimates of the likely dietary exposure of dairy cattle and hens were 2.9 and 7 ppm in the diet respectively, or 43.4 and 1.05 mg/animal/day.

The lowest feeding levels in both studies were 10 ppm in the diet. Continuous feeding at 10 ppm in the diet of dairy cattle led to total clethodim residues of <0.15 mg/kg in muscle and fat. The residues in liver and kidney were <0.16 and <0.151 mg/kg respectively. In milk the total residues were <0.0375 mg/kg over the 28-day period of the feeding study. As the highest exposure of dairy cattle is estimated as one third of the lowest level in the feeding study, it is expected that residues

above the limit of determination would not be found in milk or cattle tissues. The method of analysis for the determination of clethodim and metabolites in milk and bovine tissues is a common moiety or non-specific method, and the limits of determination in tissues and milk would be 0.2* and 0.05* mg/kg respectively. In the compound-specific method, the limit of determination was reported as 0.04 mg/kg in milk and 0.2 mg/kg in tissues. Therefore on the basis of the limits of determination in both specific and non-specific methods, MRLs of 0.05* mg/kg can be recommended for milk and 0.2* mg/kg for cattle tissues and offal; STMRs of 0 were estimated for both tissues and milk. Withdrawal of dosing at the 10 ppm level for 2-3 days led to residues below the limit of determination in all tissues.

Similarly in hens, the lowest residue level in the feed was 10 ppm. Continuous feeding at that level for 28 days resulted in residues below the limit of determination in all tissues and eggs. In the compound-specific method, the limit determination in eggs was reported as 0.05 mg/kg and in tissues as 0.2 mg/kg. However in the non-specific common moiety method used in the feeding study, the limits of determination were 0.15 mg/kg in both eggs and tissues. On the basis of the specific method, MRLs of 0.05* mg/kg are recommended for eggs and 0.2* mg/kg for poultry meat and offal. STMRs of 0 were estimated for eggs, poultry meat and poultry offal.

Processing studies on canola (rape seed), cotton, peanuts, soya beans, sugar beet, sunflowers and tomatoes were reported. Calculated processing factors were 0.22 and 0.1 for crude and edible cotton seed oil respectively, 0.4 and 0.09 for crude and refined peanut oil 0.32, for crude rape seed oil, and 0.09 and 0.002 for crude and refined soya bean oil respectively. STMRs for cotton seed, rape seed and soya beans had not previously been estimated, so STMRs for the processed products could not be calculated.

An STMR of 0.35 mg/kg was estimated for tomatoes in the 1997 review of clethodim. STMRs of 0.27, 1.2 and 0.77 were calculated for tomato juice, paste and purée respectively from the corresponding processing factors.

An STMR of 1.3 was estimated for peanuts in 1997. STMRs of 0.52 and 0.12 respectively were calculated for crude and edible peanut oil.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulfoxides and sulfones, expressed as clethodim.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
VD 0071	Beans (dry)	2	0.1 [1]	0.81
AL 0061	Bean fodder (hay)	10	–	1.8
AL 1030	Bean forage (green)	5	–	1.5
MO 1280	Cattle, kidney	W	0.2*	–
MO 1281	Cattle, liver	W	0.2*	–
MM 0812	Cattle meat	W	0.5*	–
ML 0812	Cattle milk	W	0.1*	–
PE 0840	Chicken eggs	W	0.5*	–
PM 0840	Chicken meat	W	0.5*	–

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
MO 0105	Edible offal (mammalian)	0.2*	–	0
PE 0112	Eggs	0.05*	–	0
MM 0095	Meat (from mammals other than marine mammals)	0.2*	–	0
ML 0106	Milks	0.05*	–	0
OC 0697	Peanut oil, crude			0.52
OR 0697	Peanut oil, edible			0.12
VR 0589	Potato[2]	0.5	0.2	
PO 0111	Poultry, edible offal of	0.2*	–	0
PM 0110	Poultry meat	0.2*	–	0
SO 0702	Sunflower seed	0.5	0.2 [1]	0.06
OC 0702	Sunflower seed oil, crude	0.1*	0.05 [1]	0.012
JF 0448	Tomato juice			0.27
	Tomato paste			1.2
	Tomato purée			0.77

[1] Withdrawal was recommended by the 1997 JMPR
[2] STMR could not be estimated as previously received data were not re-submitted

Note. Previous recommendations for cattle milk, meat and offal have been changed to general recommendations for mammalian commodities as it is unlikely that residues would be detectable in other livestock which are exposed to treated feed items. The highest exposure to treated feed items is for beef and dairy cattle; exposure of pigs and goats is lower.

FURTHER WORK OR INFORMATION

Desirable

Data on residues occurring in commerce and/or at consumption (from 1994 and 1997 Meetings).

DIETARY RISK ASSESSMENT

Chronic intake

In the current evaluation, STMRs for 16 commodities have been estimated. Where consumption data were available these STMRs were used in the estimates of dietary intake together with existing STMRs and a revised estimated maximum residue level for potato.

Estimated Dietary Intakes for the five GEMS/Food regional diets, based on new and existing STMRs and a proposed MRL, were in the range of 3-30% of the ADI (Annex III). The Meeting concluded that the intake of residues of clethodim resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The Meeting concluded that an acute RfD for clethodim is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard, and residues are therefore unlikely to present an acute risk to consumers.

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DIAZINON (022)

EXPLANATION

The organophosphorus insecticide diazinon was evaluated by the 1993 JMPR as a periodic review for plant protection uses. The Meeting recommended an increase in the CXL for pome fruits and cabbage from 0.5 to 2 mg/kg, and the withdrawal of the CXLs for animal commodities in the absence of animal transfer studies and data from uses to control ectoparasites. The 1995 CCPR decided to retain these CXLs (milk, meat of cattle, pigs and sheep) until new data on animal feeding trials had been reviewed by the 1996 JMPR as the governments of Australia and the manufacturer had already provided the data (ALINORM 95/24A, para 76).

The 1996 JMPR considered new feeding studies with poultry and cattle, as well as new and previously submitted data from supervised trials of ectoparasite control in cattle and sheep. That Meeting was able to estimate a number of maximum residue levels for animal products, but listed modern dipping and spraying trials on sheep and cattle at maximum GAP rates and with multiple applications as desirable.

The 1998 CCPR noted that animal transfer studies would become available in 1999 (ALINORM 99/24, para 39).

The present Meeting received information on GAP and reports of new residue trials on sheep (dipping) and pigs (spraying). Additional residue data for pome fruit and cabbage were also available.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Hubbard *et al.* (1990) developed analytical method AG-550A to determine residues of diazinon, diazoxon[1] and hydroxydiazinon[2] in cabbage and pome fruit. In this method 20 g samples are blended with acetone/water and filtered. The aqueous filtrate is extracted with petroleum ether and methylene chloride and the dried organic phase is concentrated. Diazinon and the metabolites are determined by gas chromatography with flame photometric detection. Untreated samples were fortified with 0.01-10 mg/kg diazinon, diazoxon and hydroxydiazinon. The average recoveries were as shown below.

Sample	Recovery, %		
	diazinon	diazoxon	hydroxydiazinon
Cabbage	94 ± 11	93 ± 12	99 ± 11
Apples	90 ± 6	83 ± 11	91 ± 10
Pears	93 ± 11	88 ± 11	95 ± 12

[1] diazoxon: diethyl 2-isopropyl-6-methylpyrimidin-4-yl phosphate
[2] hydroxydiazinon: *O*,*O*-diethyl- *O*-[2-(1-hydroxy-1-methylethyl)-6-methylpyrimidin-4-yl] phosphorothioate

Smal and Adams (1996) extended method AG-550A to determine residues of diazinon in organs and tissues of sheep by modifying the clean-up procedures and chromatography.

Before analysis, samples of fat were individually homogenised with dry ice to give a coarse powder. Muscle was analysed as a mixture of equal parts of tenderloin and hindquarter, and fat as a mixture of renal and subcutaneous samples.

Muscle, liver and kidney were extracted by maceration with aqueous acetone, the supernatant was filtered, the extract partitioned into methylene chloride and the solvent evaporated. Muscle samples were further cleaned up on a Bond Elut CN cartridge and liver and kidney on a Sep-Pak Florisil cartridge. Fats were extracted with hexane and the extract partitioned into acetonitrile. The acetonitrile was evaporated and the residue cleaned up on a Sep-Pak Florisil cartridge. Determination was by GLC with an NPD.

The LOD for the modified method was 0.01 mg/kg for all samples. The recoveries at this level were precise and accurate (Table 1).

Table 1. Recoveries of diazinon from fortified control tissues (Smal and Adams, 1996).

Sample	Fortification, mg/kg	Number	Recovery, %	Mean	SD	cv, %
Muscle	0.01	8	79-131	104	19	18
	0.02	7	78-106	95	9	10
	0.05	4	84-110	102	12	12
Kidney	0.01	6	86-118	104	11	11
	0.02	5	96-116	106	7	7
Liver	0.01	5	106-119	110	5	5
	0.02	4	81-99	94	9	9
Fat	0.01	4	92-105	98	6	6
	0.02	2	97, 99	98	-	-
	0.05	1	110	-	-	-
	0.1	3	78-93	87	8	9
	0.2	2	76, 89	82	-	-
	0.5	1	101	-	-	-
	1.0	1	92	-	-	-

Walser *et al.* (1996) used the modified method AG-550A to determine diazinon in pig tissues after spraying. Control specimens of muscle, liver and kidney were fortified with 0.005, 0.05, 0.1 or 0.5 mg/kg diazinon. The recoveries ranged from 81 to 123% (mean 96%. n = 48, SD 11.5 %). The LOD was 0.005 mg/kg.

Walser (1998) determined hydroxydiazinon and diazoxon by the modified method AG-550A. Control specimens of muscle, liver and kidney were spiked at 0.005 and 0.05 mg/kg and fat + skin at 0.01 and 0.1 mg/kg (Table 2). The mean recoveries from all substrates at all fortification levels were hydroxydiazinon 88%, SD 13.3%, n = 9; diazoxon 86%, SD 18.8%, n = 9.

Table 2. Recoveries of hydroxydiazinon and diazoxon from fortified control tissues (Walser, 1998).

Sample	Fortification, mg/kg	Recoveries, %	
		hydroxydiazinon	diazoxon
Muscle	0.005	89	81
	0.05	103	113
Kidney	0.005	84	74
	0.05	65	65
Liver	0.005	87	74
	0.05	77	77
Fat + skin	0.01	93, 96	89, 105
	0.1	99	99

Stability of pesticide residues in stored analytical samples

An interim report on the stability of diazinon, hydroxydiazinon and diazoxon in stored analytical samples of muscle, liver, fat and milk of sheep (Walser, 1999) gave the analytical results from a storage period of 9 months, summarized in Tables 3 and 4. The final report will be issued after a storage period of 24 months.

Table 3. Storage stability in of diazinon, diazoxon and hydroxydiazinon in sheep fat fortified with 0.2 mg/kg (Walser, 1999).

Months stored	Residues in stored specimen, mg/kg		
	diazinon	hydroxydiazinon	diazoxon
0	0.18	0.21	0.17
4	0.22	0.21	0.21
6.5	0.20	0.20	0.19
9	0.21	0.24	0.2

Table 4. Storage stability in of diazinon, diazoxon and hydroxydiazinon in milk, liver and muscle of sheep fortified with 0.1 mg/kg (Walser, 1999).

Months stored	Residues in stored specimen, mg/kg								
	Diazinon			hydroxydiazinon			diazoxon		
	Milk	Liver	Muscle	Milk	Liver	Muscle	Milk	Liver	Muscle
0	0.093	0.091	0.079	0.1	0.094	0.102	0.096	<0.02	0.071
4	0.084	0.086	0.131	0.11	0.097	0.102	0.067	<0.02	0.019
6.5	0.092	0.103	0.092	0.098	0.097	0.097	0.058	<0.02	<0.02
9	0.099	0.099	0.077	0.093	0.098	0.094	0.052	-	-

USE PATTERN

Diazinon is an insecticide with a broad spectrum of activity against a wide range of sucking, chewing and boring insects, including soil-living insects. It is used for plant protection as a foliar or soil spray or applied as a granule to the soil, and for the control of ectoparasites in sheep and pigs.

Table 5 shows the use patterns which have recently been approved in the USA for applications to pome fruits and cabbage. Uses on pome fruits are against aphids, maggots, crawlers and moths. The maximum single use rate is limited to 2.2 kg ai/ha with spray concentrations from 0.06 kg ai/hl in 3740 l water/ha to 0.235 kg ai/hl in 935 l water/ha, with a maximum total of 6.7 kg ai/ha per season in an unspecified number of applications at 14-day intervals. In cabbage the critical GAP on the label is one pre-plant treatment at an application rate of 4.6 kg ai/ha plus five foliar treatments with a maximum rate of 0.61 kg ai/ha at 7-day intervals.

Table 5. Registered uses of diazinon on pome fruits and cabbage in the USA.

Crop	Form.	Application				PHI, days
		Method	Rate, kg ai/ha	Spray conc., kg ai/ha	No.	
Cabbage	50 WP	Broadcast or drench transplant water treatment before planting. Incorporate into soil	0.56-1.6 or 2.2-3.3 or 2.3-4.6	0.0005-0.0022	1	21
		Ground treatments. Apply to plant beds 1-2 days before planting and incorporate into soil	1.1		1	21
		Ground treatments. Apply as insects occur, at least 7 days between applications	0.28-0.56 or 0.31- 0.61		1- 5	21
Pears[1]	50 WP	Foliar spray, apply at pre-pink stage	1.1-2.2	0.03-0.06	1-3[2]	21
		Foliar spray, first application in April	2.2	0.06	3[2]	21

Crop	Form.	Application				PHI, days
		Method	Rate, kg ai/ha	Spray conc., kg ai/ha	No.	
Pome fruit[1]	50 WP	Apply as dormant or delayed dormant spray	2.2	0.06 (+ 2 l oil)	1	21
		Apply early in season when crawlers first appear	2.2	0.06	1- 2[2]	21
		Foliar spray, apply beginning at petal fall, as infestations develop	2.2	0.06	1- 2[2]	21
		Foliar spray, beginning at pink stage	2.2	0.06	3[2]	21
		Foliar spray, apply when infestations first occur	2.2	0.06	3[2]	21
		Foliar spray, apply when flies are active and laying eggs	2.2	0.06	3[2]	21

[1] Label instruction: Maximam use rate per application = 2.2 kg ai/ha with a total of 6.7 kg ai/ha per season.
[2] Do not repeat application after less than 14 days

Table 6 shows the new information submitted to the 1999 JMPR on pending GAP for veterinary medicinal products containing diazinon (for further uses see the 1996 JMPR residue evaluation).

Table 6. Planned uses of diazinon in animal health (GAP pending).

Animal	Country	Application			Rate per treatment	
		Method	No.	SI/MI[1], days	mg ai/kg bw	mg ai/animal
Sheep	Registration in the EU is in progress	Dip or spray, all ages. Dip once for 1 minute with complete immersion of the animal at least once	1	35/21	Not identified	Dipping: nominal concentration in the bath 300 mg/l
		Spray	1	35/21	Approx. 24-48	2-4 l of spray per animal, nominal concentration of the spray 600 mg/l
Pigs	Registration in EU in progress	Spray, all ages	Up to three (dependent on the parasite)	28	Approx. 6	1 l of a 600 mg/l solution per animal

[1] SI: slaughter interval, MI: milking interval

RESIDUES RESULTING FROM SUPERVISED TRIALS

Uses as insecticide on plants

Pome fruit (Table 7). Supervised residue trials (12 on apples, 14 on pears) were conducted in the USA according to US GAP (max. 2.2 kg ai/ha, with 0.235 kg ai/hl, 935 l water/ha to 0.06 kg ai/hl, 3741 l water/ha per application; max. 6.7 kg ai/ha per season, PHI 21 days). The trials were on duplicate plots. Samples were analysed for diazinon, diazoxon and hydroxydiazinon. The residues of hydroxydiazinon were all below the LOD of 0.01 mg/kg.. Double-underlined residues are from treatments according to GAP and are valid for estimating maximum residue levels and STMRs. If the residues at 28 days were higher than those at the GAP PHI of 21 days, the higher values were used for evaluation. Although all trials included control plots, no control results are recorded in the Tables as the residues were all below the LOD. The samples were deep frozen before analysis for 4-7 months.

Table 7. Residues of diazinon and diazoxon from supervised trials on apples and pears in the USA (Ross and Hackett, 1992a).

Report no. Report date Location	Dates of treatment	Application rate per treatment			Growth stage at last treatment	Sample	Phi, days	Residues, mg/kg	
		kg ai/ha	water l/ha	kg ai/hl				diazinon	diazoxon
02-IR-003-91 A	19.08.91	1.5	2805	0.053	fruit 6 cm	apple	21	0.02	<0.01
28.09.92	02.09.91	1.5	2805	0.053				<0.01	<0.01
Fresno County,	16.09.91	1.5	2805	0.053			28	<0.01	<0.01
California			(3741)	(0.04) [1]				<0.01	<0.01
02-IR-003-91 B	19.08.91	2.2	2805	0.078	fruit 6 cm	apple	21	0.01	<0.01
28.09.92	02.09.91	2.2	2805	0.078				0.01	<0.01
Fresno County,	16.09.91	2.2	2805	0.078			28	<0.01	<0.01
California			(3741)	(0.058)[1]				<0.01	<0.01
05-IR-004-91 A	05.08.91	1.7	977	0.17	fruit	apple	22	0.06	<0.01
28.09.92	22.08.91	1.7	977	0.17	6-8 cm			0.03	<0.01
Columbia County,	04.09.91	1.7	977	0.17			28	0.01	<0.01
New York			(3741)	(0.044)[1]				0.02	<0.01
05-IR-004-91 B	05.08.91	2.2	977	0.23	fruit	apple	22	0.03	<0.01
28.09.92	22.08.91	2.2	977	0.23	6-8 cm			0.02	<0.01
Columbia County,	04.09.91	2.2	977	0.23			28	0.04	<0.01
New York			(3741)	(0.06)[1]				0.01	<0.01
05-IR-004-91 C	05.08.91	4.5	977	0.46	fruit	apple	22	<0.01	<0.01
28.09.92	22.08.91	4.5	977	0.46	6-8 cm				
Columbia County,	04.09.91	4.5	977	0.46			28	0.04	<0.01
New York			(3741)	(0.12)[1]					
OS-IR-602-91 A	27.06.91	1.7	1945	0.087	pre-harvest	apple	21	0.03	<0.01
28.09.92	11.07.91	1.7	1945	0.087				0.04	<0.01
Johnston County,	25.07.91	1.7	1945	0.087			28	<0.01	<0.01
N. Carolina			(3741)	(0.045)[1]				0.02	<0.01
OS-IR-602-91 B	27.06.91	2.2	1945	0.11	pre-harvest	apple	21	0.05	<0.01
28.09.92	11.07.91	2.2	1945	0.11				0.08	<0.01
Johnston County,	25.07.91	2.2	1945	0.11			28	0.01	<0.01
N. Carolina			(3741)	(0.057)[1]				<0.01	<0.01
OS-IR-602-91 C	27.06.91	4.5	1945	0.23	pre-harvest	apple	21	0.10	<0.01
28.09.92	11.07.91	4.5	1945	0.23					
Johnston County,	25.07.91	4.5	1945	0.23			28	0.07	<0.01
N. Carolina			(3741)	(0.12)[1]					
OW-IR-621-91 A	01.08.91	1.7	2151	0.079	fruit	apple	21	0.08	<0.01
28-09.92	17.08.91	1.7	2151	0.079	6-7 cm			0.06	<0.01
Yakima County,	30.08.91	1.7	2151	0.079			28	0.05	<0.01
Washington			(3741)	(0.045)[1]				0.08	<0.01
OW-IR-621-91 B	01.08.91	2.2	2151	0.10	fruit	apple	21	0.11	<0.01
28-09.92	17.08.91	2.2	2151	0.10	6-7 cm			0.13	<0.01
Yakima County,	30.08.91	2.2	2151	0.10			28	0.24	<0.01
Washington			(3741)	(0.057)[1]				0.18	<0.01
OW-IR-621-91 C	01.08.91	4.5	2151	0.21	fruit	apple	21	0.42	<0.01
28-09.92	17.08.91	4.5	2151	0.21	6-7 cm				
Yakima County,	30.08.91	4.5	2151	0.21			28	0.32	<0.01
Washington			(3741)	(0.12)[1]					
OW-IR-622-91 A	01.08.91	1.7	2151	0.079	fruit	apple	21	0.13	<0.01
28.09.92	17.08.91	1.7	2151	0.079	6-6.5 cm			0.13	<0.01
Yakima County,	30.08.91	1.7	2151	0.079			28	0.10	<0.01
Washington			(3741)	(0.045)[1]				0.07	<0.01
OW-IR-622-91 B	01.08.91	2.2	2151	0.10	fruit	apple	21	0.06	<0.01
28-09.92	17.08.91	2.2	2151	0.10	6-6.5 cm			0.10	<0.01
Yakima County,	30.08.91	2.2	2151	0.10			28	0.05	<0.01
Washington			(3741)	(0.057)[1]				0.03	<0.01
NE-IR-103-91 A	31.07.91	1.7	2806	0.061	immature	apple	21	0.04	<0.01
28.09.92	14.08.91	1.7	2806	0.061	fruit			<0.01	<0.01
Allegan County,	28.08.91	1.7	2806	0.061			28	0.02	<0.01
Michigan			(3741)	(0.046)[1]				0.04	<0.01
NE-IR-103-91 B	31.07.91	2.2	2806	0.078	immature	apple	21	0.03	<0.01
28.09.92	14.08.91	2.2	2806	0.078	fruit			0.03	<0.01
Allegan County,	28.08.91	2.2	2806	0.078			28	0.04	<0.01

Report no. Report date Location	Dates of treatment	Application rate per treatment			Growth stage at last treatment	Sample	Phi, days	Residues, mg/kg	
		kg ai/ha	water l/ha	kg ai/hl				diazinon	diazoxon
Michigan			(3741)	(0.059)[1]				0.04	<0.01
02-IR-004-91 A	17.07.91	1.7	2806	0.061	fruit	pear	21	<0.01	<0.01
28.09.92	31.07.91	1.7	2806	0.061	7.5 cm			<0.01	<0.01
Fresno County,	14.08.91	1.7	2806	0.061	diameter		28	<0.01	<0.01
California			(3741)	(0.046)[1]				<0.01	<0.01
02-IR-004-91 B	17.07.91	2.2	2806	0.078	fruit	pear	21	<0.01	<0.01
28.09.92	31.07.91	2.2	2806	0.078	7.5 cm			<0.01	<0.01
Fresno County,	14.08.91	2.2	2806	0.078	diameter		28	<0.01	<0.01
California			(3741)	(0.059)[1]				<0.01	<0.01
02-IR-004-91 C	17.07.91	4.5	2806	0.16	fruit	pear	21	0.02	<0.01
28.09.92	31.07.91	4.5	2806	0.16	7.5 cm				
Fresno County,	14.08.91	4.5	2806	0.16	diameter		28	<0.01	<0.01
California			(3741)	(0.12)[1]					
OW-IR-118-91 A	16.07.91	1.7	468	0.36	fruit	pear	21	0.04	<0.01
28.09.92	30.07.91	1.7	468	0.36	5.5-6 cm			0.02	<0.01
Washington	13.08.91	1.7	468	0.36	diameter		28	0.04	<0.01
County, Oregon			(3741)	(0.045)[1]				0.04	<0.01
OW-IR-118-91 B	16.07.91	2.2	468	0.47	fruit	pear	21	0.04	<0.01
28.09.92	30.07.91	2.2	468	0.47	5.5-6 cm			0.04	<0.01
Washington	13.08.91	2.2	468	0.47	diameter		28	<0.01	<0.01
County, Oregon			(3741)	(0.059)[1]				0.02	<0.01
OW-IR-118-91 C	16.07.91	4.5	468	0.96	fruit	pear	21	0.04	<0.01
28.09.92	30.07.91	4.5	468	0.96	5.5-6 cm				
Washington	13.08.91	4.5	468	0.96	diameter		28	0.02	<0.01
County, Oregon			(3741)	(0.12)[1]					
OW-IR-201-91 A	07.06.91	1.7	652	0.26	mature	pear	21	<0.01	<0.01
28.09.92	21.06.91	1.7	1188	0.14	fruit			<0.01	<0.01
Stanislaus	05.07.91	1.7	1291	0.13			28	<0.01	<0.01
County,			(3741)	(0.045)[1]				<0.01	<0.01
California									
OW-IR-201-91 B	07.06.91	2.2	652	0.34	mature	pear	21	<0.01	<0.01
28.09.92	21.06.91	2.2	1188	0.18	fruit			<0.01	<0.01
Stanislaus	05.07.91	2.2	1291	0.17			28	<0.01	<0.01
County,			(3741)	(0.059)[1]				<0.01	<0.01
California									
OW-IR-201-91 C	07.06.91	4.5	652	0.69	mature	pear	21	<0.01	<0.01
28.09.92	21.06.91	4.5	1188	0.38	fruit				
Stanislaus	05.07.91	4.5	1291	0.35			28	<0.01	<0.01
County,			(3741)	(0.12)[1]					
California									
OW-IR-623-91 A	02.07.91	1.7	935	0.18	green fruit	pear	21	<0.01	<0.01
28.09.92	17.07.91	1.7	935	0.18				<0.01	<0.01
Yakima County,	30.07.91	1.7	935	0.18			28	<0.01	<0.01
Washington			(3741)	(0.045) [1]				<0.01	<0.01
OW-IR-623-91 B	02.07.91	2.2	935	0.24	green fruit	pear	21	<0.01	<0.01
28.09.92	17.07.91	2.2	935	0.24				0.02	<0.01
Yakima County,	30.07.91	2.2	935	0.24			28	<0.01	<0.01
Washington			(3741)	(0.06) [1]				<0.01	<0.01
OW-IR-624-91 A	20.07.91	1.7	2151	0.079	fruit	pear	21	0.05	<0.01
28.09.92	01.08.91	1.7	2151	0.079	5-6 cm			0.11	<0.01
Yakima County,	17.08.91	1.7	2151	0.079			28	0.11	0.02
Washington			(3741)	(0.045)[1]				0.11	0.01
OW-IR-624-91 B	20.07.91	2.2	2151	0.10	fruit	pear	21	0.11	<0.01
28.09.92	01.08.91	2.2	2151	0.10	5-6 cm			0.11	0.01
Yakima County,	17.08.91	2.2	2151	0.10			28	0.07	0.01
Washington			(3741)	(0.057)[1]				0.12	0.01
OW-IR-624-91 C	20.07.91	4.5	2151	0.21	fruit	pear	21	0.43	0.02
28.09.92	01.08.91	4.5	2151	0.21	5-6 cm		28	0.26	0.02
Yakima County,	17.08.91	4.5	2151	0.21					
Washington			(3741)	(0.12)[1]					
NE-IR-104-91 A	24.06.91	1.7	2806	0.061	immature	pear	21	0.05	<0.01
28.09.92	08.07.91	1.7	2806	0.061	fruit			0.06	<0.01

Report no. Report date Location	Dates of treatment	Application rate per treatment			Growth stage at last treatment	Sample	Phi, days	Residues, mg/kg	
		kg ai/ha	water l/ha	kg ai/hl				diazinon	diazoxon
Allegan County, Michigan	22.07.91	1.7	2806 (3741)	0.061 (0.046)[1]			28	0.06 <0.01	<0.01 <0.01
NE-IR-104-91 B 28.09.92 Allegan County, Michigan	24.06.91 08.07.91 22.07.91	2.2 2.2 2.2	2806 2806 2806 (3741)	0.078 0.078 0.078 (0.059)[1]	immature fruit	pear	21 28	0.01 <u>0.11</u> <0.01 <0.01	<0.01 <0.01 <0.01 <0.01
NE-IR-401-91 A 28.09.92 Wayne County, New York	10.07.91 24.07.91 07.08.91	1.7 1.7 1.7	935 935 935 (3741)	0.18 0.18 0.18 (0.045) [1]	fruit 5.2-5.6 cm	pear	21 28	<<u>0.01</u> <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01
NE-IR-401-91 B 28.09.92 Wayne County, New York	10.07.91 24.07.91 07.08.91	2.2 2.2 2.2	935 935 935 (3741)	0.24 0.24 0.24 (0.06) [1]	fruit 5.2-5.6 cm	pear	21 28	<<u>0.01</u> <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01
NE-IR-401-91 C 28.09.92 Wayne County, New York	10.07.91 24.07.91 07.08.91	4.5 4.5 4.5	935 935 935 (3741)	0.48 0.48 0.48 (0.12) [1]	fruit 5.2-5.6 cm	pear	21 28	0.01 <0.01	<0.01 <0.01

[1]kg ai/hl calculated for 3741 l water/ha (water volume according to label instructions)

<u>Head cabbages</u> (Table 8). Eleven supervised residue trials on cabbage according to the current US label directions in seven states of the USA (representing 72% of the US cabbage production) were reported. The directions allow for a single pre-planting treatment of 4.4 kg ai/ha followed by five post-emergence foliar applications of 0.55 kg ai/ha at 7-day intervals using ground equipment. In general, the trials were on duplicate plots. The samples were deep frozen for 4-12 months before analysis. All samples were analysed for diazinon, diazoxon and hydroxydiazinon. Hydroxydiazinon was not found in any sample, and diazoxon was detected only in 2 samples of trimmed heads (trial 02-IR-002-91). Single- and double-underlined residues are from treatments according to GAP. Single-underlined residues are valid for estimation of the maximum residue level. Double-underlined residues (in trimmed heads) were used to estimate the STMR. Although all trials included control plots, no control results are recorded in the Tables as the residues were all below the LOD.

Table 8. Residues of diazinon from supervised trials on cabbages in the USA (Ross and Hackett, 1992b).

Report no. Report date Location	Form. Variety	Dates of treatment	Application rate per treatment			Sample	PHI, days	Diazinon, mg/kg
			kg ai/ha	water l/ha	kg ai/hl			
NE-IR-201-91 A 23.09.92 Fayette County, Ohio	14 GR + 50 WP Prize	17.05.91 03.07.91 11.07.91 17.07.91 24.07.91 31.07.91	4.5 0.56 0.56 0.56 0.56 0.56	 213 214 229 221 232	 0.26 0.26 0.245 0.25 0.24	heads, untrimmed	7 7 14 14 21 21	0.07 0.24 0.04 0.01 <0.01 <u>0.01</u>
						heads, trimmed	7 7 14 14 21 21	<0.01 <0.01 <0.01 <0.01 <<u>0.01</u> <0.01
						wrapper leaves	7 7 14 14 21 21	0.19 0.51 0.09 0.07 0.04 0.06

Report no. Report date Location	Form. Variety	Dates of treatment	Application rate per treatment			Sample	PHI, days	Diazinon, mg/kg
			kg ai/ha	water l/ha	kg ai/hl			
NE-IR-201-91 B 23.09.92 Fayette County, Ohio	14 GR + AG 500 Prize	17.05.91 03.07.91 11.07.91 17.07.91 24.07.91 31.07.91	4.5 0.56 0.56 0.56 0.56 0.56	 213 214 229 221 232	 0.26 0.26 0.245 0.25 0.24	heads, untrimmed heads, trimmed wrapper leaves	7 7 14 14 21 21 7 7 14 14 21 21 7 7 14 14 21 21	0.11 0.30 <0.01 0.03 <0.01 <0.01 <0.01 0.01 <0.01 <0.01 <0.01 <0.01 0.35 0.34 0.09 0.21 0.05 0.10
02-IR-002-91 A 23.09.92 Fresno County, California	14 GR + 50 WP Copen- hagen MKT.	11.04.91 15.05.91 22.05.91 29.05.91 05.06.91 12.06.91	4.5 0.56 0.56 0.56 0.56 0.56	 468 468 468 468 468	 0.12 0.12 0.12 0.12 0.12	heads, untrimmed heads, trimmed wrapper leaves	8 8 14 14 21 21 8 8 14 14 21 21 8 8 14 14 21 21	0.13 (<0.01)[1] 0.09 (<0.01) 0.02 (<0.01) 0.01 (<0.01) <u>0.01</u> (<0.01) <0.01 (<0.01) <0.01 (<0.01) <0.01 (<0.01) <0.01 (0.01) <0.01 (<0.01) <<u>0.01</u> (<0.01) <0.01 (<0.01) 0.21 (<0.01) 0.10 (<0.01) 0.03 (<0.01) 0.05 (<0.01) 0.03 (<0.01) 0.04 (<0.01)
02-IR-002-91 B 23.09.92 Fresno County, California	AG 500 + 50 WP Copen- hagen MKT.	11.04.91 15.05.91 22.05.91 29.05.91 05.06.91 12.06.91	4.5 0.56 0.56 0.56 0.56 0.56	 468 468 468 468 468	 0.12 0.12 0.12 0.12 0.12	heads, untrimmed heads, trimmed wrapper leaves	8 8 14 14 21 21 8 8 14 14 21 21 8 8 14 14 21 21	0.10 (<0.01) 0.05 (<0.01) 0.05 (<0.01) 0.03 (<0.01) <<u>0.01</u> (<0.01) <0.01 (<0.01) <0.01 (<0.01) <0.01 (<0.01) <0.01 (<0.01) <0.01 (<0.01) <<u>0.01</u> (0.02) <0.01 (<0.01) 0.28 (<0.01) 0.12 (<0.01) 0.08 (<0.01) 0.04 (<0.01) 0.03 (<0.01) 0.02 (<0.01)

Report no. Report date Location	Form. Variety	Dates of treatment	Application rate per treatment			Sample	PHI, days	Diazinon, mg/kg
			kg ai/ha	water l/ha	kg ai/hl			
05-IR-002-91 A 23.09.92 Columbia County, New York	14 GR + AG 500 Market Price	06.06.91 07.08.91 14.08.91 21.08.91 28.08.91 05.09.91	4.5 0.56 0.56 0.56 0.56 0.56	 702 702 702 702 702	 0.080 0.080 0.080 0.080 0.080	heads, untrimmed	7 7 13 13 21 21	0.36 0.13 0.05 0.15 <u>0.08</u> 0.02
						heads, trimmed	7 7 13 13 21 21	<0.01 <0.01 <0.01 <0.01 <<u>0.01</u> <0.01
						wrapper leaves	7 7 13 13 21 21	0.55 0.78 0.24 0.25 0.11 0.13
05-IR-002-91 B 23.09.92 Columbia County, New York	14 GR + AG 500 Market Price	06.06.91 07.08.91 14.08.91 21.08.91 28.08.91 05.09.91	9.0 1.1 1.1 1.1 1.1 1.1	 702 702 702 702 702	 0.16 0.16 0.16 0.16 0.16	heads, untrimmed	7 13 21	1.1 0.31 0.34
						heads, trimmed	7 13 21	<0.01 <0.01 <0.01
						wrapper leaves	7 13 21	1.6 0.43 0.31
07-IR-002-91 A 23.09.92 Indian River County, Florida	14 GR + AG 500 Bravo	23.10.91 29.11.91 06.12.91 13.12.91 20.12.91 27.12.91	4.5 0.56 0.56 0.56 0.56 0.56	 468 468 468 468 468	 0.12 0.12 0.12 0.12 0.12	heads, untrimmed	7 7 14 14 21 21	0.33 0.52 0.22 0.30 <u>0.35</u> 0.24
						heads, trimmed	7 7 14 14 21 21	0.04 0.02 <0.01 <0.01 <<u>0.01</u> <0.01
						wrapper leaves	7 7 14 14 21 21	3.2 2.7 1.8 1.2 0.51 1.0

Report no. Report date Location	Form. Variety	Dates of treatment	Application rate per treatment			Sample	PHI, days	Diazinon, mg/kg
			kg ai/ha	water l/ha	kg ai/hl			
07-IR-002-91 B 23.09.92 Indian River County, Florida	AG 500 + AG 500 Bravo	23.10.91 29.11.91 06.12.91 13.12.91 20.12.91 27.12.91	4.5 0.56 0.56 0.56 0.56 0.56	 468 468 468 468 468	 0.12 0.12 0.12 0.12 0.12	heads, untrimmed	7 7 14 14 21 21	0.69 0.55 0.27 0.12 0.25 0.26
						heads, trimmed	7 7 14 14 21 21	0.09 0.03 <0.01 0.01 <0.01 <0.01
						wrapper leaves	7 7 14 14 21 21	2.8 3.6 1.4 1.1 0.65 0.91
OS-IR-303-91 A 23.09.92 Cameron County, Texas	14 GR + AG 500 Solid Blue 760/ Abbott	12.06.90 22.03.91 29.03.91 05.04.91 12.04.91 19.04.91	4.5 0.56 0.56 0.56 0.56 0.56	 203 203 203 203 203	 0.28 0.28 0.28 0.28 0.28	heads, untrimmed	7 7 15 15 21 21	0.15 0.17 0.03 0.04 0.03 0.05
						heads, trimmed	7 7 15 15 21 21	0.01 0.09 <0.01 <0.01 <0.01 <0.01
						wrapper leaves	7 7 15 15 21 21	0.47 0.42 0.23 0.24 0.07 0.07
OS-IR-303-91 B 23.09.92 Cameron County, Texas	14 GR + AG 500 Solid Blue 760/ Abbott	12.06.90 22.03.91 29.03.91 05.04.91 12.04.91 19.04.91	9.0 1.1 1.1 1.1 1.1 1.1	 203 203 203 203 203	 0.55 0.55 0.55 0.55 0.55	heads, untrimmed	7 15 21	0.54 0.12 0.16
						heads, trimmed	7 15 21	0.04 0.01 <0.01
						wrapper leaves	7 15 21	2.1 1.4 0.42

Report no. Report date Location	Form. Variety	Dates of treatment	Application rate per treatment			Sample	PHI, days	Diazinon, mg/kg
			kg ai/ha	water l/ha	kg ai/hl			
OS-IR-601-91 A 23.09.92 Franklin County, N. Carolina	14 GR + 50 WP Market Price	22.02.91 17.04.91 24.04.91 01.05.91 08.05.91 15.05.91	4.5 0.56 0.56 0.56 0.56 0.56	 359 359 359 359 359	 0.16 0.16 0.16 0.16 0.16	heads, untrimmed	7 7 14 14 21 21	0.16 0.20 <0.01 <0.01 <0.01 <0.01
						heads, trimmed	7 7 14 14 21 21	0.07 0.07 <0.01 <0.01 <0.01 <0.01
						wrapper leaves	7 7 14 14 21 21	0.41 0.59 0.02 0.03 <0.01 <0.01
OS-IR-601-91 B 23.09.92 Franklin County, N. Carolina	AG 500 + 50 WP Market Price	22.02.91 17.04.91 24.04.91 01.05.91 08.05.91 15.05.91	4.5 0.56 0.56 0.56 0.56 0.56	 359 359 359 359 359	 0.16 0.16 0.16 0.16 0.16	heads, untrimmed	7 7 14 14 21 21	0.09 0.04 0.02 0.02 <0.01 <0.01
						heads, trimmed	7 7 14 14 21 21	0.07 0.08 <0.01 <0.01 <0.01 <0.01
						wrapper leaves	7 7 14 14 21 21	0.91 0.85 0.14 0.13 0.07 0.11
MW-IR-701-91 A 23.09.92 Columbia County, Wisconsin	AG 500 + AG 500 Little Rock	21.05.91 03.07.91 10.07.91 17.07.91 24.07.91 31.07.91	4.5 0.56 0.56 0.56 0.56 0.56	 187 187 187 187 187	 0.30 0.30 0.30 0.30 0.30	heads, untrimmed	7 7 14 14 21 21	0.97 0.57 0.20 0.31 0.24 0.19
						heads, trimmed	7 7 14 14 21 21	0.01 0.09 <0.01 <0.01 <0.01 <0.01
						wrapper leaves	7 7 14 14 21 21	1.2 1.3 1.9 1.1 0.86 0.86

Report no. Report date Location	Form. Variety	Dates of treatment	Application rate per treatment			Sample	PHI, days	Diazinon, mg/kg
			kg ai/ha	water l/ha	kg ai/hl			
MW-IR-701-91	AG 500 +	21.05.91	9.0			heads,	7	1.9
B	AG 500	03.07.91	1.1	187	0.60	untrimmed	14	0.48
23.09.92		10.07.91	1.1	187	0.60		21	0.53
Columbia	Little	17.07.91	1.1	187	0.60			
County,	Rock	24.07.91	1.1	187	0.60	heads,	7	0.05
Wisconsin		31.07.91	1.1	187	0.60	trimmed	14	<0.01
							21	<0.01
						wrapper	7	4.7
						leaves	14	2.7
							21	2.2

[1] In parentheses: diazoxon

Uses as ectoparasiticide on domestic animals

New trials on sheep and pigs were conducted according to pending GAP with the Neocidal 600 EW formulation which is not yet on the market. This formulation is a micro-emulsion of oil in water, containing 60% diazinon in the oil phase, intended to replace the former generation of EC formulations.

Smal and Adams (1996) treated sheep by dipping. Dip samples were analysed for diazinon by reversed-phase HPLC. Six replicate analyses yielded a mean concentration of 309 mg/l with a cv of 2%. The results of the trial are shown in Table 9.

No. and species: 46 sheep (25% Merino, 25% Border Leicester and 50% Dorset)
Body weight: 31.4-49.8 kg
Treatment: Plunge dipping for 1 minute in a bath containing 300 mg diazinon per litre
Slaughter intervals: 8 sheep were slaughtered 2, 4, 6, 8 or 10 weeks after treatment; 6 controls
Samples analysed: Muscle (equal weights of tenderloin and hindquarter), liver, kidney, renal and subcutaneous fat
LOD: 0.01 mg/kg in all samples

Table 9. Residues of diazinon in tissues of sheep (Smal and Adams, 1996).

Slaughter after	Animal No.	Diazinon, mg/kg			
		Muscle	Kidney	Liver	Fat
2 weeks	9397	0.05	0.03	<0.01	1.2
	9426	0.06	0.02	<0.01	1.2
	9428	0.04	0.02	<0.01	1.2
	9419	0.02	0.02	<0.01	0.6
	9388	0.05	0.03	<0.01	1.1
	9425	0.05	0.02	<0.01	1.4
	9399	0.06	0.02	<0.01	1.5
	9405	0.05	0.02	<0.01	1.1
4 weeks	9392	0.02	0.01	not analysed	0.41
	9394	0.01	<0.01		0.30
	9402	0.01	<0.01		0.32
	9391	0.02	<0.01		0.40
	9411	0.02	<0.01		0.29
	9424	<0.01	<0.01		0.16
	9400	0.01	<0.01		0.22
	9422	0.02	<0.01		0.41
6 weeks	9420	<0.01	<0.01	not analysed	0.10
	9409	<0.01	<0.01		0.11
	9417	0.01	<0.01		0.15
	9406	<0.01	<0.01		0.14

Slaughter after	Animal No.	Diazinon, mg/kg			
		Muscle	Kidney	Liver	Fat
	9423	<0.01	<0.01		0.11
	9427	<0.01	<0.01		0.08
	9396	0.01	<0.01		0.18
	9430	<0.01	<0.01		0.08
8 weeks	9401	<0.01			0.02
	9418	<0.01			0.03
	9395	<0.01			0.03
	9386	<0.01	not analysed	not analysed	0.04
	9414	<0.01			0.03
	9407	<0.01			0.03
	9421	<0.01			0.04
	9398	<0.01			0.03
10 weeks	9403				0.01
	9389				0.02
	9390				0.02
	9415	not analysed	not analysed	not analysed	0.02
	9387				0.02
	9393				0.02
	9412				0.03
	9416				0.01

Adams and Cheung (1998) analysed samples from the trial by Smal and Adams (1996) which had been deep frozen from April 1996 for diazinon, hydroxydiazinon and diazoxon in December 1997. Studies of stability in frozen storage (Tables 3 and 4) indicate that diazinon would be unstable in muscle, kidney and liver.

Table 10. Residues of diazinon, diazoxon and hydroxydiazinon in sheep tissues taken 2 weeks after dipping and analysed after prolonged frozen storage (Adams and Cheung, 1998).

Animal no.	Residues of diazinon and metabolites, mg/kg								
	Muscle			Kidney			Liver		
	diazinon	diazoxon	hydroxy-diazinon	diazinon	diazoxon	hydroxy-diazinon	diazinon	diazoxon	hydroxy-diazinon
9388	0.08 (0.05)[1]	<0.01	<0.01	0.02 (0.03)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9397	0.11 (0.05)	<0.01	<0.01	0.02 (0.03)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9399	0.12 (0.06)	<0.01	<0.01	0.02 (0.02)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9405	0.04 (0.05)	<0.01	<0.01	0.01 (0.02)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9419	0.02 (0.02)	<0.01	<0.01	<0.01 (0.02)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9425	0.05 (0.05)	<0.01	<0.01	0.02 0.02	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9426	0.06 (0.06)	<0.01	<0.01	<0.01 (0.02)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01
9428	0.04 (0.04)	<0.01	<0.01	0.02 (0.02)	<0.01	<0.01	<0.01 (<0.01)	<0.01	<0.01

[1]Residues in parentheses: original analyses (Table 9)

Table 11. Residues of diazinon, diazoxon and hydroxydiazinon in sheep fat analysed after prolonged storage (Adams and Cheung, 1998).

Slaughter after	Animal no.	Residues, mg/kg						
		fat[1]	renal fat			subcutaneous fat		
		diazinon	diazinon	diazoxon	hydroxydiazinon	diazinon	diazoxon	hydroxydiazinon
2 weeks	9388	1.1	1.1	<0.01	0.01	0.76	<0.01	0.02
	9397	1.2	1.2	<0.01	0.02	0.89	<0.01	0.02
	9399	1.5	1.6	<0.01	0.01	1.00	<0.01	0.02
	9405	1.1	1.2	<0.01	<0.01	0.70	<0.01	<0.01
	9419	0.6	0.71	<0.01	<0.01	0.47	<0.01	<0.01
	9425	1.4	1.4	<0.01	0.01	1.0	<0.01	0.02
	9426	1.2	1.1	<0.01	0.01	0.87	<0.01	0.01
	9428	1.2	1.4	<0.01	0.01	0.94	<0.01	0.01
4 weeks	9391	0.40	0.43	<0.01	<0.01	0.35	<0.01	<0.01
	9392	0.41	0.49	<0.01	<0.01	0.41	<0.01	<0.01
	9394	0.30	0.35	<0.01	<0.01	0.32	<0.01	<0.01
	9400	0.22	0.31	<0.01	<0.01	0.19	<0.01	<0.01
	9402	0.32	0.39	<0.01	<0.01	0.28	<0.01	<0.01
	9411	0.29	0.42	<0.01	<0.01	0.27	<0.01	<0.01
	9422	0.41	0.41	<0.01	<0.01	0.39	<0.01	<0.01
	9424	0.16	0.22	<0.01	<0.01	0.14	<0.01	<0.01

[1] Original analyses (Table 9) of combined renal and subcutaneous fat

Following a controlled drug-free period of seven days, Walser *et al.* (1996) sprayed pigs twice (Table 12) with Neocidol 600 EW.

No. and species: 42 Dutch Landrace (including 2 controls); equal numbers of females and castrated males
Body weight: 68-96.1 kg
Treatment: 2 spray applications in an interval of 7 days. Each pig was sprayed separately with 1 litre of a spray solution containing 600 mg diazinon per litre, taking care to wet the entire body
Slaughter intervals: 8 pigs slaughtered 1, 3, 7, 14 or 21 days after second treatment. 2 controls slaughtered before first treatment
Samples analysed: muscle (equal weights of tenderloin and hindquarter), liver, kidney, skin with subcutaneous fat (natural proportion)
LOD (diazinon): tissues 0.005 mg/kg, blood 0.005 mg/l, fat and skin 0.01 mg/kg

Table 12. Residues of diazinon in pigs sprayed twice (Walser *et al.*, 1996).

Days after 2nd treatment	Diazinon, mg/kg				
	Muscle	Liver	Kidney	Fat and skin	Blood
1	0.035	0.022	<0.005	0.25	<0.005
3	0.025	0.027	<0.005	0.12	<0.005
7	0.015	0.014	<0.005	0.03	<0.005
14	0.012	0.009	<0.005	<0.01	<0.005
21	0.007	0.006	<0.005	<0.01	<0.005

Samples from the trial by Walser *et al.* which were deep frozen in June/July1996 were analysed for hydroxydiazinon and diazoxon in September 1998 (Walser, 1998) .

Residues of hydroxydiazinon and diazoxon in all the samples were below the LOD, i.e. <0.005 mg/kg in muscle, liver and kidney and <0.01 mg/kg in skin + subcutaneous fat.

Bioequivalence of EC and EW formulations

The new residue trials on sheep and pigs were with the new EW formulation (microemulsion of 60% diazinon in water) instead of the EC formulations which were used in all previous trials (see JMPR 1996), which were based on organic solvents. The manufacturer therefore conducted comparison trials to show the bioequivalence of Neocidol 600 EW and the EC formulations Neocidol 600 EC (A-3695 J), Neocidol 250 EC (A-7182A) and Topclip Gold Shield (A-139 F).

Morrison (1994) compared the levels of diazinon in the blood and fat after spraying sheep with the 3 solvent-based formulations (Tables 13 and 14).

Animals:	18 male white sheep
Body weight:	36.5 ± 4 kg
Formulation used:	group A: Neocidol 250 EC (A-7182 A) group F: Topclip Gold Shield (A-139 F) group J: Neocidol 600 EC (A-3695 J)
Treatment:	each side of the animal sprayed for 1 min with 3 l of spray emulsion of a nominal diazinon concentration of 600 mg/l. After spraying, each animal was allowed to stand for 10-15 min. to drain excess emulsion.
Sampling:	blood samples were taken 48 and 24 hours before treatment and 1, 2, 4, 8, 12, 24 and 48 hours and 3, 5, 7, 9, 14, 21 and 28 days after treatment. fat samples of 2.5-6 g were taken by biopsy of the fat depot at the base of the tail 8 and 28 days after treatment.
LOD of diazinon:	0.005 mg/kg for both fat and blood

Table 13. Concentration of diazinon in blood of sprayed sheep (Morrison, 1994).

Time	Diazinon, mg/l, group mean ± standard deviation		
	Group A	Group F	Group J
- 48 h	<0.006	<0.006	<0.006
- 24 h	<0.006	<0.006	<0.006
+ 1 hr	0.0092 ± 0.0007	0.012 ± 0.0053	0.015 ± 0.0025
+ 2 h	0.014 ± 0.0033	0.013 ± 0.0033	0.017 ± 0.004
+ 4 h	0.019 ± 0.0065	0.025 ± 0.0064	0.024 ± 0.0072
+ 8 h	0.028 ± 0.0053	0.03 ± 0.0064	0.029 ± 0.0087
+ 12 h	0.028 ± 0.0063	0.027 ± 0.0049	0.026 ± 0.0066
+ 24 h	0.023 ± 0.0032	0.023 ± 0.0027	0.023 ± 0.0049
+ 48 h	0.024 ± 0.0042	0.024 ± 0.003	0.023 ± 0.0042
+ 3 days	0.027 ± 0.0033	0.027 ± 0.0065	0.024 ± 0.003
+ 5 days	0.017 ± 0.0023	0.016 ± 0.0049	0.016 ± 0.003
+ 7 days	0.011 ± 0.0023	0.013 ± 0.0034	0.01 ± 0.0015
+ 9 days	0.008 ± 0.0013	0.01 ± 0.0017	0.008 ± 0.0015
+ 14 days	0.0051 ± 0.0001	0.006 ± 0.0004	0.005 ± 0.0002
+ 21 days	<0.006	<0.006	<0.006
+ 28 days	<0.006	<0.006	<0.006

Table 14. Concentration of diazinon in fat of sprayed sheep (Morrison, 1994).

Days after treatment	Diazinon, mg/kg, group mean ± standard deviation		
	Group A	Group F	Group J
8	2.66 ± 0.83	2.2 ± 0.8	1.9 ± 0.25
28	0.15 ± 0.07	0.16 ± 0.05	0.12 ± 0.06

Strittmatter *et al.* (1996) determined the levels of diazinon in the blood and wool after spraying sheep with 3 different formulations including the 600 EW (Tables 15 and 16).

Species used:	21 male white sheep
Body weight:	33 ± 4 kg
Formulations:	group 1: Neocidol 600 EW (A-8265 B) group 2: Topclip Gold Shield (A-139 F) group 3: Neocidol 600 EC (A-3695 J)
Treatment:	each animal was individually plunge-dipped for 1 min in 180 l dip containing 300 mg/l of diazinon. The dip bath was prepared for each animal of each group
Sampling:	blood samples were taken 24 hours before treatment and 1, 2, 4, 8, 12, 24 and 48 hours and 3, 5, 7, 9, 14 and 20 days after treatment wool samples were taken 2, 7, 14 and 20 days after treatment from 6 different sites on each sheep and pooled within the treatment group skin samples without the fleece (3 x 3 cm) were cut and homogenised fat samples were homogenised. Subcutaneous samples were 100–250 g from the back and shoulders; omental and kidney fat samples were combined in equal portions (200-500 g)
LOD (diazinon):	0.005 mg/l in blood, 600 mg/kg in wool

The dip solutions were sampled before and after dipping each sheep and analysed for diazinon.

The results were evaluated statistically. For blood and wool the area under the concentration/time curve (AUC), the maximum concentration (C_{max}) and the time of maximum concentration (T_{max}) were determined. Table 15 shows the individual results, group geometric means and ranges of the AUC, C_{max} and T_{max} for diazinon concentrations in the blood.

Table 15. Diazinon in blood of sprayed sheep (Strittmatter *et al.*, 1996).

Formulation	Animal no.	AUC	C_{max}, mg/l	T_{max}, days
A-8265 B	1584	6.76	0.048	1
	1590	5.86	0.050	12
	1594	7.45	0.051	12
	1215	5.38	0.048	12
	1517	6.41	0.045	8
	1620	5.45	0.058	8
	1639	6.50	0.041	12
	Geom. mean	6.22	0.048	7.49
	Range	5.38-7.45	0.041-0.058	1-12
A-0139 F	1574	6.79	0.034	12
	1582	6.33	0.056	8
	1597	5.46	0.052	12
	1600	5.89	0.041	48
	1611	6.34	0.044	8
	1624	7.78	0.051	4
	1626	8.61	0.080	12
	Geom. mean	6.67	0.050	11.14
	Range	5.46-8.61	0.034-0.080	4-48
A-3695 J	1591	5.87	0.043	12
	1595	4.67	0.032	12
	1596	6.42	0.046	12
	1598	5.37	0.039	12
	1622	5.73	0.108	8
	1635	5.84	0.061	12
	1638	6.16	0.051	12
	Geom. mean	5.7	0.050	11.33
	Range	4.67-6.42	0.032-0.108	8-12

The mean ratios of C_{max} and AUC for A-8265B to the corresponding values for A-0139F and 3695J, together with the probability P that these ratios (μ) are between 0.7 and 1.3[3], are shown below.

Ratio μ for	AUC	P[0.7≤ μ≤ 1.3]	C_{max}	P[0.7≤ μ≤ 1.3]
A-8265 B/A-0139 F	0.93	0.998	0.96	0.983
A-8265 B/A-3695 J	1.09	0.994	0.96	0.933

This statistical analysis indicated that formulation A-8265 B is bioequivalent to both formulations A-0139 F and A-3695 J.

Table 16. Diazinon in wool of sprayed sheep (Strittmatter *et al.*, 1996).

Formulation	Animal no.	AUC	C_{max}, mg/l	T_{max}, days
A-8265 B	1584	111150	9920	2
	1590	103625	7730	2
	1594	108000	8260	2
	1215	87845	6420	2
	1517	87125	6540	2
	1620	91775	6960	2
	1639	104215	7530	2
	Geom. mean	98671	7546	2.0
	Range	87125-111150	6420-9920	
A-0139 F	1574	98500	9510	2
	1582	108190	7730	2
	1597	105345	8470	2
	1600	94330	7410	2
	1611	109440	8630	2
	1624	145260	10600	2
	1626	149465	10700	2
	Geom. mean	114091	8926	2.0
	Range	94330-149465	7410-10700	
A-3695 J	1591	115350	8550	2
	1595	91435	6280	2
	1596	116890	8780	2
	1598	94450	8050	2
	1622	101420	8110	2
	1635	105910	8140	2
	1638	113385	8680	2
	Geom. mean	105118	8042	2.0
	Range	91435-116890	6280-8780	

The mean ratios of C_{max} and AUC in wool for A-8265 B to the values in the other two formulations are as shown below.

Ratio μ for	AUC	P[0.7≤ μ≤ 1.3]	C_{max}	P[0.7≤ μ≤ 1.3]
A-8265B/A-0139 F	0.86	0.990	0.85	0.983
A-8265B/A-3695 J	0.94	0.999	0.94	0.999

Again the results show that formulation A-8265 B is bioequivalent to both the other formulations.

[3] The formulation F_2 is considered to be bioequivalent to the formulation F_1 if the function f (F_2) = f (F_1) ± 30% (Fühler, H., *et al.*, 1983).

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Apples and pears (Table 17). Apples from the North Carolina field trial OS-IR-602-91 and pears from the New York field trial NE-IR-401-91 harvested at a PHI of 21 days were processed in the laboratory using typical household procedures. Samples were analysed for diazinon, hydroxydiazinon and diazoxon. Hydroxydiazinon and diazoxon were not detected. Processing factors were also derived from the processing study reported by the 1993 JMPR (trial OW-IR-618-88).

Table 17. Diazinon residues in apples and pears and their processed fractions.

Crop Trial Treatment	Sample	PHI, days	Diazinon, mg/kg	Processing factor	Report no. Reference
Apples OW-IR-618-88 7 x 3.36 kg ai/ha	Fruit	0	0.98		JMPR 1993
	Culls		2.2	2.24	
	Pomace, wet		1.4	1.43	Ross and Gold, 1989
	Pomace, dry		0.02	0.02	
	Juice, fresh		<0.01	<0.01	
	Juice, canned		<0.01	<0.01	
	Slices, canned		<0.01	<0.01	
	Slices, frozen		<0.01	<0.01	
	Apple sauce		<0.01	<0.01	
Apples, OS-IR-602-91 3 x 2.2 kg ai/ha	Fruit, unwashed (RAC)	21	0.04		ABR-92017
	Fruit, washed		0.02	0.5	
	Wash water		<0.01	<0.25	Ross and Hackett, 1992a
	Fruit cores		0.02	0.5	
	Peel, washed		0.32	8	
	Fruit, peeled and washed		<0.01	<0.25	
	Fruit, sliced and baked		<0.01	<0.25	
	Whole fruit, baked		0.05	1.25	
Apples OS-IR-602-91 3 x 4.4 kg ai/ha	Fruit, unwashed (RAC)	21	0.07		
	Fruit, washed		0.1	1.4	
	Wash water		<0.01	<0.14	
	Fruit cores		0.02	0.29	
	Peel, washed		0.43	6.1	
	Fruit, peeled and washed		<0.01	<0.14	
	Fruit, sliced and baked		<0.01	<0.14	
	Whole fruit, baked		0.08	1.1	
Pears NE-IR-401-91 3 x 2.2 kg ai/ha	Fruit, unwashed (RAC)	21	<0.01		ABR-92017
	Fruit, washed		<0.01		Ross and Hackett, 1992a
	Wash water		<0.01		
	Fruit cores		<0.01		
	Peel, washed		0.01		
	Fruit, peeled and washed		<0.01		
	Fruit, sliced and baked		<0.01		
	Whole fruit, baked		<0.01		
Pears NE-IR-401-91 3 x 4.4 kg ai/ha	Fruit, unwashed (RAC)	21	<0.01		
	Fruit, washed		0.02		
	Wash water		<0.01		
	Fruit cores		<0.01		
	Peel, washed		0.07		

Crop Trial Treatment	Sample	PHI, days	Diazinon, mg/kg	Processing factor	Report no. Reference
	Fruit, peeled and washed		<0.01		
	Fruit, sliced and baked		<0.01		
	Whole fruit, baked		<0.01		

Residues in the edible portion of food commodities

Diazinon residues in peeled and washed, and in sliced and baked apples were below the LOD of 0.01 mg/kg (Table 17).

Diazinon residues were below the LOD (<0.01 mg/kg) in trimmed heads of cabbages treated with 4.6 kg ai/ha pre-planting followed by 5 post-emergence foliar applications of 0.56 kg ai/ha after a PHI of 21 days (Table 8).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The 1996 JMPR asked for monitoring data on fat of sheep. The current Meeting received the 1998 UK statutory surveillance results for kidney fat (231 samples of cattle, 330 of pig, 610 of sheep). Only one sample of sheep kidney fat contained residues of diazinon, at 2.3 mg/kg (Anon., 1998).

APPRAISAL

Diazinon was evaluated by the 1993 JMPR as a periodic review for plant protection uses. The 1993 Meeting recommended an increase in the CXL for pome fruits and cabbages from 0.5 to 2 mg/kg and the withdrawal of the CXLs for animal commodities in the absence of animal processing studies and data from uses to control ectoparasites.

The 1996 Meeting considered new feeding studies with poultry and cattle, and new and previously reported data from supervised trials of ectoparasite control in cattle and sheep. That Meeting was able to estimate a number of maximum residue levels but considered additional information on GAP and modern trials at maximum GAP rates to be highly desirable.

The Meeting received reports of new residue trials on sheep (dipping) and pigs (spraying). Additional results for pome fruit and cabbage were also available.

The analytical methods that determine the parent compound as well as the metabolites diazoxon and hydroxydiazinon rely on acetone/water extraction and liquid-liquid partition, followed in extracts of animal products by clean-up on various cartridges, with determination by GLC with an FPD or NPD. The LODs of the three compounds were 0.005 mg/kg in pig blood, muscle, liver and kidney and 0.01 mg/kg in cabbage, apples, pears, pig skin and fat, and sheep tissues.

The 1993 JMPR noted that residues of diazinon *per se* are generally stable in crop samples (except strawberries) and processed commodities for a minimum of 26 months under freezer conditions (-27° to -12°C). Hydroxydiazinon was stable in crops except strawberries and apples. Residues of diazoxon however were unstable in all substrates tested except maize oil.

Residues of diazinon and hydroxydiazinon are stable in animal tissues and milk under deep frozen conditions ($\leq$-18°C) for at least 9 months, but diazoxon is only stable in fat, of limited stability in milk and highly unstable in liver and muscle

Definition of the residue

The residue was defined by the 1993 JMPR as diazinon *per se*. The current Meeting discussed the relevance of metabolites to the dietary intake. Metabolism in plants progresses, as in animals, primarily by hydrolysis of the ester linkage, yielding 4-hydroxy-2-isopropyl-6-methylpyrimidine, followed by oxidation of the isopropyl group to primary and tertiary alcohols and/or oxidation of the methyl group to the alcohol. Diazoxon and hydroxydiazinon were not reported as significant plant metabolites by the 1993 JMPR but could play an intermediary role in the degradation of diazinon and so could be of concern for the assessment of acute dietary risk.

In all, 120 samples of pome fruit and 225 samples of cabbage were analysed with freezer storage of pome fruit for 4-7 months and cabbage for 4-12 months. Diazoxon was found in 8 samples of pome fruit (5.7%) and in 2 of cabbage (0.89%) with a maximum value of 0.02 mg/kg in both commodities. Hydroxydiazinon could not be determined in any sample. The disappearance of the metabolites under freezer conditions indicates that they will also be unstable under field conditions. Furthermore, the Meeting was informed that 19 trials with snap beans, apples, plums and carrots had been conducted to investigate the occurrence of diazoxon and hydroxydiazinon at harvest, without storage of the samples before analysis. The first results showed residues of the metabolites well below 10% of the parent. The Meeting therefore concluded that diazoxon and hydroxydiazinon would not be of concern for consumer exposure and that the residue in plants for dietary intake estimations should be defined as diazinon.

In animal products, residues of diazoxon and hydroxydiazinon were below the LODs in muscle, kidney, liver and blood samples at all periods after dosing. In the 32 sheep fat samples analysed no diazoxon could be determined, but hydroxydiazinon was found in 12 samples (37.5%) at two weeks after treatment (max. 0.02 mg/kg). At the slaughtering interval according to GAP of four weeks, no residues of either metabolite were found. The absence of diazoxon in samples of animal tissues (except fat) stored deep frozen could be due to its absence at slaughter or to its rapid degradation. However, no diazoxon residues were found in sheep fat (where it is stable), whereas diazinon and hydroxydiazinon were detected. Although the determination of diazoxon is limited by its instability in certain tissues, it can be assumed that it occurs at much lower levels than diazinon, and any remaining small amounts of diazoxon at the time of slaughter can reasonably be expected to be rapidly hydrolysed. The Meeting concluded that there is no need to include diazoxon or hydroxydiazinon in the residue definition for the assessment of dietary risk of animal products.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: diazinon.

The residue is fat-soluble.

The Meeting received data from supervised trials on apples, pears and head cabbages. New dipping and spraying studies were carried out on sheep and pigs.

Pome fruit. The 2 mg/kg MRL proposed by the 1993 JMPR was based on older US results and former US GAP (2–8 x 0.06 kg ai/hl, PHI 14 days). Recently US GAP for diazinon on pome fruit was changed to a maximum of 2.2 kg ai/ha, 0.235 kg ai/hl per application, and a maximum of 6.7 kg ai/ha per season, PHI 21 days. No other information on GAP was reported (obsolete uses reported by the 1993 JMPR were not considered).

Twelve supervised trials on apples and 14 on pears in the USA complied with the new US GAP. Samples were analysed for residues of diazinon, diazoxon and hydroxydiazinon.

The residues in apples and pears from trials according to current US GAP in rank order (median underlined) were <0.01 (7), 0.01, 0.02 (2), 0.04 (6), 0.06 (2), 0.08 (2), 0.10, 0.11 (2), 0,12, 0.13 and 0.24 mg/kg.

Hydroxydiazinon was not found in any of the samples. Diazoxon was detected in pears from two trials according to GAP at 0.01 and 0.02 mg/kg.

On the basis of the combined apple and pear data, the Meeting estimated an STMR of 0.04 mg/kg and a maximum residue level of 0.3 mg/kg for pome fruit to replace the existing CXL (2 mg/kg).

Diazinon residues were below the LOD of 0.01 mg/kg in washed, peeled and sliced apples. Processing factors of 1.43, <0.01, <0.01 and <0.01 for wet apple pomace, juice, canned slices and apple sauce respectively, were derived from a processing study reported by the 1993 JMPR. From the STMR of 0.04 mg/kg, the Meeting estimated STMRs of 0.0572 mg/kg for wet apple pomace, and 0.0004 mg/kg for apple juice, sauce and canned slices.

Head cabbages. The 2 mg/kg MRL for cabbages proposed by the 1993 JMPR was based on US data and former US GAP (4.4 kg ai/ha followed by >1 x 0.56 kg ai/ha, PHI 5–7 days). The US GAP was recently changed to an increased PHI of 21 days.

Eleven supervised trials on cabbages according to current US label use directions were reported. These directions allow for a single pre-plant treatment of 4.4 kg ai/ha followed by five post-emergence foliar applications of 0.55 kg ai/ha at 7-day intervals using ground equipment.

The samples analysed were described in the report as follows: “Untrimmed and trimmed cabbage heads were obtained from separate plants, ... in order to avoid contamination. Trimmed cabbage heads were obtained by removing the wrapper leaves consisting of the obviously decomposed outer leaves.” The Meeting noted that the term “trimmed heads” should be in accordance to the Codex definition for the commodity, but concluded that maximum residue levels should not be based on cabbages with outer leaves removed as there is so much uncertainty as to how many leaves would be removed in practice.

The diazinon residues in rank order were <0.01, <0.01, 0.01, 0.01, 0.05, 0.08, 0.24 and 0.35 mg/kg for untrimmed heads, <0.01 (11) mg/kg for trimmed heads and 0.04, 0.07, 0.1, 0.1, 0.11, 0.13, 0.86 and 1.0 mg/kg for wrapper leaves.

Diazoxon was detected (0.02 mg/kg) in only one trial, in trimmed heads at a PHI of 21 days. Hydroxydiazinon was not found at or above the LOD.

The Meeting estimated a maximum residue level of 0.5 mg/kg for diazinon in head cabbages, to replace the existing CXL (2 mg/kg). An STMR of 0.01 mg/kg was estimated on the basis of the results for trimmed heads,.

Animal products. An EW formulation of diazinon, which is planned to replace the former EC-type formulations, was used in new trials on sheep dipping and pig spraying, but GAP is only pending. However, bioequivalence studies have shown that the water-based EW formulation used in the new studies is equivalent to the EC formulations used in earlier studies.

Sheep. According to the use pattern reported by the 1996 JMPR, the most important treatment rates recommended are 250 mg ai/l for sheep dipping (uses range from100 to 600 mg ai/l). The new dipping trial was conducted according to New Zealand GAP (200-400 mg ai/l) using a bath concentration of 300 mg/l.

The highest residues of diazinon occurred at the earliest slaughtering interval of two weeks. Fat contained the highest residues (maximum 1.5, median 1.2, mean 1.16 mg/kg). Low residues were found in muscle (maximum 0.06, median 0.05, mean 0.0475 mg/kg) and kidney (maximum 0.03, median 0.02, mean 0.0225 mg/kg). No residues were detected in the liver. The residues in muscle and kidney dissipated quickly, with all samples being below the LOD of 0.01 mg/kg by 8 and 6 weeks

respectively. In fat diazinon was more persistent, with low residues up to 0.03 mg/kg present 10 weeks after treatment. The data confirm the findings reported by the 1996 JMPR (evaluation p. 216) for sheep: muscle maximum 0.03, median 0.02; liver maximum 0.01, median <0.01; kidney maximum 0.02, median 0.02; omental fat maximum 1.3, median1.1; subcutaneous fat maximum 1.4, median 1.4 mg/kg.

Residues of diazoxon were not found in any of the sheep tissues tested. Low levels of hydroxydiazinon were found in four of eight animals in subcutaneous fat and in one of eight animals in renal fat from sheep slaughtered 2 weeks after treatment (maximum 0.02 mg/kg). The residues were below the LOD of 0.01 mg/kg by 4 weeks after treatment.

Pigs. Diazinon residues in the muscle of pigs sprayed twice decreased from 0.035 mg/kg one day after the 2nd treatment to 0.007 mg/kg after 21 days. In liver, a maximum of 0.027 mg/kg was found after 3 days which decreased to 0.006 mg/kg at day 21. The highest residues of 0.25 mg/kg in the fat and skin were found on day 1 and decreased to <0.01 mg/kg on day 14. In kidney and blood, residues were below the LOD of 0.005 mg/kg in all samples. Neither diazoxon nor hydroxydiazinon was detected in any samples.

No new studies were reported on cattle or goats.

The new data on dipped sheep and sprayed pigs reported to the Meeting do not differ from the data provided in earlier submissions.

The 1996 JMPR had noted that in practice some animals might be exposed to more than one type of treatment (e.g. spraying and dipping as well as ear tags or wound dressing), but the present Meeting was informed that multiple treatments are unlikely in practice.

The 1996 JMPR requested monitoring data on subcutaneous fat of sheep. The Meeting received the 1998 UK statutory surveillance results for kidney fat (231 samples from cattle, 330 from pigs, 610 from sheep). Only one sample of sheep kidney fat contained residues of diazinon (2.3 mg/kg).

The Meeting agreed to maintain the previous maximum residue level estimates for the liver, kidney and meat of cattle, goats, pigs and sheep of 0.03, 0.03 and 2 mg/kg in the fat respectively. The STMRs estimated on the basis of different uses (dip, ear tag, spray) on goats, pigs, cattle and sheep by the 1996 JMPR were confirmed.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels and STMRs shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: diazinon.

The residue is fat-soluble.

Commodity		Recommendation		
		MRL, mg/kg		STMR
CCN	Name	New	Previous	mg/kg
JF 0226	Apple juice			0.0004
	Apple pomace, wet			0.057
	Apple sauce			0.0004
	Apple slices, canned			0.0004
VB 0041	Cabbages, Head	0.5	2	0.01

Commodity		Recommendation		
		MRL, mg/kg		STMR
CCN	Name	New	Previous	mg/kg
MM 0814	Goat meat	2 (fat) V	2 (fat) V	0.3 (fat) [1] 0.02 (whole muscle) [1]
MO 0098	Kidney of cattle, goats, pigs and sheep	0.03 V	0.03 V	0.01[1]
MO 0099	Liver of cattle, goats, pigs and sheep	0.03 V	0.03 V	0.01[1]
MM 0097	Meat of cattle, pigs and sheep	2 (fat) V	2 (fat) V	0.3 (fat) [1] 0.02 (whole muscle) [1]
ML 0106	Milks	0.02 F V	0.02 F V	0.02[1]
FP 0009	Pome fruits	0.3	2	0.04

[1]Estimated by the 1996 JMPR

FURTHER WORK OR INFORMATION

Studies on fruits and vegetables to investigate the occurrence of diazoxon and hydroxydiazinon at harvest, without storage of samples before analysis.

DIETARY RISK ASSESSMENT

Chronic intake

STMRs have been estimated by the current Meeting for pome fruit and head cabbages as well as by the 1996 JMPR for tomatoes and animal products. Where consumption data were available these STMRs were used in the estimates of dietary intake together with the existing MRLs and draft MRLs for 38 other food commodities.

The dietary intakes for the five GEMS/Food regional diets, based on new and existing STMRs and MRLs, were in the range of 20% to 180% of the ADI. The Meeting concluded that the dietary intake of diazinon residues may exceed the ADI for two GEMS/Food regional diets (Annex III). Further refinements of dietary intake estimates will be undertaken during the next periodic review of residues.

Acute intake

The international estimate of short-term intake (IESTI) for diazinon was calculated for the commodities for which MRLs and STMRs were established and for which consumption data (large portion consumption and unit weight) were available. The results are shown in Annex IV. The IESTI varied from 0.004 to 0.008 mg/kg bw in the general population and from 0.016 to 0.028 mg/kg in children. As no acute reference dose has been established the acute risk assessment for diazinon was not finalized.

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DINOCAP (087)

EXPLANATION

Dinocap was evaluated in 1998 when residue data on grapes, apples, cucurbits, strawberries, peppers, peaches, apricots and tomatoes were submitted. Recommendations were made for all commodities except apricots and tomatoes. The Meeting re-evaluated data on tomatoes submitted in 1998 in the light of new information provided on GAP in Spain.

USE PATTERN

The registered use on tomatoes in Spain is 0.0195-0.026 kg ai/hl of an EC formulation, with a PHI of 7 days.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The residues of dinocap in tomatoes from trials reviewed by the 1998 JMPR which approximated the Spanish GAP of 0.0195-0.026 kg ai/hl and PHI of 7 days are shown in Table 1.

Table 1. Residues from supervised trials on tomatoes reviewed by 1998 JMPR.

Country, year	Formulation	Field or glasshouse	Application			PHI, days	Residues, mg/kg
			No.	kg ai/ha	kg ai/hl		
France (South), 1997	EC	F	4	0.29-0.36	0.021	7	<0.05
Italy, 1992	EC	F	3	0.11	0.018	7	<0.04
Italy, 1993	WP	F	3	0.18	0.018	7	<0.04
	EC	F	3	0.17	0.018	7	<0.04
Spain, 1991	EC	F	1	0.26	0.026	8	0.04
	EC	F	2	0.26	0.026	8	<0.04
Spain, 1993	EC	G	2	0.39	0.026	8	0.18
	EC	G	3	0.39	0.025	7	0.08

APPRAISAL

Dinocap was evaluated in 1998 when residue data on grapes, apples, cucurbits, strawberries, peppers, peaches, apricots and tomatoes were submitted. Maximum residue levels were estimated for all commodities except apricots and tomatoes. In view of new information on GAP in Spain provided by the manufacturer the data on residues in tomatoes submitted in 1998 were re-evaluated.

Field trials in France, Italy and Spain according to Spanish GAP (0.0195-0.026 kg ai/hl, PHI 7 days) gave residues of <0.04 (4), <0.05 and 0.04 mg/kg at PHIs of 7 or 8 days. In two trials in glasshouses in Spain, the residues were 0.08 and 0.18 mg/kg. The residues in rank order were <0.04 (4), <0.05, 0.04, 0.08 and 0.18 mg/kg.

The Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR of 0.045 mg/kg for dinocap in tomatoes.

RECOMMENDATIONS

The Meeting estimated the maximum residue level and STMR shown below. The maximum residue level is recommended for use as an MRL.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: sum of dinocap isomers and dinocap phenols, expressed as dinocap.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
VO 0448	Tomato	0.3	-	0.045

DIETARY RISK ASSESSMENT

Chronic intake

An STMR for tomato was estimated for dinocap by the present Meeting. At the 1998 JMPR, dinocap was evaluated as a new compound and STMRs were estimated for apples, grapes, strawberries, peaches, peppers and cucurbits. The dietary intake was calculated for all the commodities.

The International Estimated Daily Intakes (IEDIs) for the five GEMS/Food regional diets, based on new and existing STMRs, were in the range of 0 to 2% of the ADI. The Meeting concluded that the intake of residues of dinocap resulting from its uses that have been considered by the JMPR is unlikely to present a public heath concern.

Acute intake

The acute reference dose for dinocap established by the 1998 JMPR is 0.008 mg/kg bw. The international estimates of short-term intake (IESTIs) for tomatoes are shown in Annex IV. The IESTI was 0.008 mg/kg bw (100% of the acute RfD) for adults and 0.0087 mg/kg for children. For the general population the Meeting concluded that it is unlikely that the acute intake of dinocap residues would exceed the acute reference dose. The acute RfD is not relevant to children because it is based on a teratogenic effect. The Meeting recommended that the JMPR re-evaluate the acute toxicity of dinocap to consider the necessity for establishing an acute RfD relevant to children.

ETHEPHON (106)

EXPLANATION

Ethephon was re-evaluated for residues in the CCPR Periodic Review Programme by the 1994 JMPR, which recommended conversion of some existing GLs to MRLs because an ADI had been established in 1993 and residue data had been provided.

The 1996 CCPR was informed that the EC would provide data on indoor trials on tomatoes according to GAP (ALINORM 97/24, para 63).

At the 1999 CCPR the Committee retained the draft MRLs for cantaloupe, grapes, peppers, pineapple and tomato at Step 7B (ALINORM 99/24 A, para 85).

The basic manufacturer provided information on analytical methods and GAP together with supplementary residue data from trials on cantaloupes, grapes, peppers, pineapples and tomatoes. Information on national registered uses and MRLs, analytical methods, and residues in food was provided by Australia, Germany, The Netherlands, Poland, Thailand and the UK. The USA provided comments on the draft MRL for pineapple and the European Commission provided reports of supervised residue trials on glasshouse tomatoes.

METHODS OF RESIDUE ANALYSIS

The Meeting received information on two GLC methods of analysis for ethephon in crops and processed commodities, a head-space procedure in which ethylene is released, and one in which ethephon is methylated with diazomethane.

Nygren (1993) described the head-space method, which was developed to provide a regulatory procedure that avoided the use of diazomethane. The ground sample is weighed into a 250 ml pressure bottle and water is added to ensure a constant head-space volume. A tartaric acid stabilizing solution is added and the capped bottle heated in a 60-65ºC water bath for one hour. Excess pressure is released and the bottle flushed with nitrogen to remove endogenous ethylene while retaining the ethephon in the stabilizing solution. Tribasic sodium phosphate is added and the bottle capped immediately and returned to the 60-65ºC water bath for 1 hour. Prepared standards are also introduced at this point. After cooling and allowing time for equilibration the head-space gas (2 ml) is analysed for ethylene by GLC with an FID. The LOD for fruits and vegetables was generally 0.01-0.02 mg/kg. The recoveries from grapes over the range 0.07-10 mg/kg were mean 104%, range 90-122%, n = 9.

Nygren (1993) validated the ethylene release method for many substrates including cereal grains and straw, sugar cane and nuts; recoveries from commodities in the supervised trials in the present evaluation are shown in Table 1. Recoveries did not appear to be related to fortification levels. The LOD for most substrates was about 0.02 mg/kg, but was somewhat higher for cereal grains and straw. Control samples contained apparent ethephon levels below the LOD (Table 1). When the method was tested for ruggedness, variations in times and temperatures in the preliminary removal of endogenous ethylene and the subsequent conversion of ethephon to ethylene had little effect on the recoveries from most substrates, but those from the more difficult samples (cereals and nuts) were affected.

Table 1. Recoveries of ethephon from 5 commodities by the ethylene release method (Nygren, 1993).

Commodity	Fortification, mg/kg	Mean recovery, %	Range, %	No. of analyses	Max apparent ethephon in controls (no. of analyses)
Tomato	0.02-2	103	96-114	20	0.0016 (4)
Pineapple	0.02-2	103	89-120	24	0.0067 (8)
Cantaloupe	0.02-2	101	93-112	24	0.0047 (8)
Green peppers	0.02-30	99	78-108	24	0.014 (8)
Grapes	0.02-2	97	89-106	24	0.0013 (7)

Fuchsbichler (1989) described a method mentioned in the 1994 JMPR residue evaluation, based on the methylation of ethephon before determination by GLC. The method was developed for use on rape seed, straw and shoots and was based on an earlier method for the analysis of barley grain and straw. Freeze-dried samples were extracted with methanol and the volume of the extract reduced in a flash evaporator. An aliquot was treated with methanolic HCl and ether and centrifuged. The supernatant liquid was reduced in volume and treated with diazomethane to methylate the ethephon. The volume was reduced under a stream of nitrogen and then adjusted for the determination of the dimethyl ethephon by GLC with an FPD. Standard solutions of ethephon were treated with diazomethane to serve as the analytical standards of dimethyl ethephon. Analytical recoveries from rape seed, straw and shoots fortified at 0.07-5.3 mg/kg were mean 93%, range 69-109%, n = 11.

Grolleau (1997) analysed grapes and their processed products by the diazomethane procedure with an LOD of 0.1 mg/kg. Analytical recoveries from grapes fortified at 0.1-2.0 mg/kg were mean 79%, range 70-93%, n = 7; from must fortified at 0.1 and 0.25 mg/kg 93% and 70%, and from wine fortified at 0.1 and 0.50 mg/kg 90% and 123%.

Nygren (1990) described the method referenced as Rhône-Poulenc (1989b) by the 1994 JMPR, that was used for ethephon residues in 52 types of sample including fruits, vegetables, coffee beans, tea, processed fruit and vegetables, seeds, nuts, sauces, juices, wine and water. Hard-frozen samples are first ground with dry ice and freeze-dried to constant weight. Fresh and dry weights are recorded so that residues can be expressed on the fresh weight. Studies with [^{14}C]ethephon had shown that no ethephon is lost during freeze-drying. The procedure is then as described above. The author warns that used glassware adsorbs ethephon very strongly in the absence of crop material, presumably because of etching during repeated cleaning in alkaline detergent. It is therefore necessary to keep standard solutions of ethephon in new glassware or polyethylene or polypropylene vessels.

In the official methods of analysis of The Netherlands (Ministry of Health, Welfare and Sport, 1996) ethephon is extracted with ethyl acetate and the extract is treated with diazomethane to produce dimethyl ethephon, which is determined by GLC with an FPD. The LOD is 0.1 mg/kg. Recoveries of 78-98% were achieved from non-fatty foods fortified with ethephon at 0.1-11 mg/kg.

USE PATTERN

The Meeting received information on the registered uses of ethephon on selected crops (Table 2).

Ethephon is a plant growth regulator, and when used on crops near maturity plant responses are associated with fruit ripening. In most cases it is better to harvest the crop at the proper stage of maturity than to set minimum pre-harvest intervals. When pre-harvest intervals are set they are normally shorter than necessary to avoid over-ripening.

The timing of application to coloured grapes (to promote uniform coloration) is different from that to Thompson Seedless (to hasten maturity).

Ethephon may also be used at an early growth stage to elicit other responses. For example treatment of pineapples about 6-8 months after planting induces flowering. The pineapples reach maturity about 6-10 months later.

The application rate (kg ai/ha) is the prime determinant of GAP. Label directions for spray concentration and volume are intended to ensure adequate coverage.

Table 2. Registered uses of ethephon on apples, bananas, cantaloupes, cereals, cherries, grapes, oilseed rape, peppers, pineapples, and tomatoes.

Crop	Country	Form	Application				PHI, days[1]
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Apples	Netherlands	SL 480 g/l	foliar	0.24-0.72	0.024-0.048	1	7
Apples	Netherlands	SL 480 g/l	foliar	0.24-2.9	0.024-0.19	1	[a]
Apples	Germany	SL 420 g/l	foliar	0.19	0.013	2	M
Apples	Germany	SL 474 g/l	foliar	0.36	0.024	1	7
Bananas	Thailand	SL 480 g/l	post-harvest		0.050-0.15	1	
Barley, spring	UK	SL	foliar	0.16-0.31		1	M
Barley, summer	Germany	SL	foliar	0.36	0.09-0.18	1	49
Barley, summer	Netherlands	SL 480 g/l	foliar	0.24		1	M
Barley, winter	Germany	SL	foliar	0.48	0.12-0.24	1	49
Barley, winter	Netherlands	SL 480 g/l	foliar	0.48-0.60		1	M
Barley, winter	UK	SL	foliar	0.16-0.48		1	M
Cantaloupes	USA	SL 240 g/l	foliar	0.84		1	2
Cherries, sweet and sour	Germany	SL 420 g/l	foliar	0.63	0.042	1	7
Grapes	Colombia	SL 480 g/l	foliar, 35 days after harvest	1.44-1.92		1	M
Grapes	Dominican Republic	SL 720 g/l	foliar	0.13-0.5		1	6
Grapes	France	SL 180 g/l	foliar	0.36-0.45		1	M
Grapes	Japan	SL 30 g/l	foliar	0.0167		1	M
Grapes	Mexico	SL 240 g/l	foliar	0.48-0.96		1	M
Grapes	Mexico	SL 480 g/l	foliar	0.48-0.96		1	M
Grapes	Taiwan	SL 480 g/l	foliar	0.14-0.192	0.008-0.010	1	M
Grapes	Thailand	SL 480 g/l	foliar		0.024-0.036	1	M
Grapes	Venezuela	SL 480 g/l	foliar		0.019-0.024	1	M
Grapes, for raisins	Greece	SL 480 g/l	foliar		0.036-0.048	1	4
Grapes, table	Australia	SL 480 g/l	foliar		0.0096-0.029	1	14
Grapes, table	Chile	SL 480 g/l	foliar	0.24-0.48		1	M
Grapes, table	Greece	SL 480 g/l	foliar		0.048-0.072	1	4
Grapes, table	USA	SL 240 g/l	foliar	0.14-0.56		1	14
Grapes, Tokay	USA	SL 240 g/l	foliar	0.28-0.56		1	14
Grapes, Barlkina variety	South Africa	SL 480 g/l	foliar		0.024		M
Grapes, Cambel variety	Korea, South	SL 480 g/l	foliar		0.02	1	M
Grapes, wine	Australia	SL 480 g/l	foliar		0.030-0.091	1	7
Grapes, wine	Italy	SL 240 g/l	foliar	0.72-0.84	0.043-0.065	1	40
Grapes, wine	Italy	SL 480 g/l	foliar	0.77-1.0	0.048-0.072	1	40
Mango	Thailand	SL 480 g/l	post-harvest		0.020-0.040	1	
Oats, winter	UK	SL	foliar	0.23		1	M
Onions, seed	Netherlands	SL 480 g/l	foliar	1.4		1	28
Peppers	Argentina	SL 480 g/l	foliar	0.96-1.9		1	20
Peppers	Greece	SL 480 g/l	foliar		0.096-0.12	1	4
Peppers	Netherlands	SL 480 g/l	foliar		0.048		3
Peppers	Portugal	SL 480 g/l	foliar	0.72-0.96		1	7
Peppers	Spain	SL 480 g/l	foliar		0.048-0.072	1 fg[b]	10

Crop	Country	Form	Application				PHI, days[1]
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Peppers	Uruguay	SL 480 g/l	foliar	0.96-1.92		1	10
Peppers	USA	SL 240 g/l	foliar	0.35-1.12		1	5
Peppers, sweet	Netherlands	SL 480 g/l	foliar	0.24-0.72	0.048	1 g	3
Pineapple, flower induction	Australia	SL 480 g/l	foliar	0.58-4.3		1 [c]	7
Pineapple, flower induction	Bolivia	SL 240 g/l	foliar	0.24-0.96		1 [c]	14
Pineapple, flower induction	Brazil	SL 240 g/l	foliar	0.24	0.048	1	14
Pineapple, flower induction	Colombia	SL 480 g/l	foliar	0.72		1	M
Pineapple, flower induction	Costa Rica	SL 480 g/l	foliar	0.24-0.96		1 [c]	7
Pineapple, flower induction	Dominican Republic	SL 480 g/l	foliar	0.72-1.2		1 [c]	M
Pineapple, flower induction	Ecuador	SL 480 g/l	foliar	0.24-0.96		1 [c]	M
Pineapple, flower induction	El Salvador	SL 480 g/l	foliar	0.24-0.96		1 [c]	7
Pineapple, flower induction	Guatemala	SL 720 g/l	pour in plant 50 ml solution		0.1-0.18	1 [c]	8
Pineapple, flower induction	Honduras	SL 480 g/l	foliar	0.24-0.96		1 [c]	7
Pineapple, flower induction	India	SL 480 g/l	foliar	0.18-0.25		1	M
Pineapple, flower induction	Indonesia	SL 480 g/l	foliar	0.24-0.48			
Pineapple, flower induction	Indonesia	SL 480 g/l	bud applic. 50 ml solution		0.024-0.048		
Pineapple, flower induction	Ivory Coast	SL 480 g/l	foliar	1.4 -2.9		1 [c]	M
Pineapple, flower induction	Japan	SL 100 g/l	foliar		0.05-0.1	1 [c]	M
Pineapple, flower induction	Malaysia	SL 100 g/l	foliar	0.17-0.27	0.017-0.022	1 [c]	M
Pineapple, flower induction	Malaysia	SL 480 g/l	foliar	0.32-0.48	0.032-0.040	1 [c]	M
Pineapple, flower induction	Mexico	SL 240 g/l	foliar	0.48-0.96		1 [c]	M
Pineapple, flower induction	Mexico	SL 480 g/l	foliar	0.48-0.96		1 [c]	M
Pineapple, flower induction	Nicaragua	SL 480 g/l	foliar	0.24-0.96		1 [c]	7
Pineapple, flower induction	Nicaragua	SL 720 g/l	foliar	0.94	0.031-0.047	1 [c]	7
Pineapple, flower induction	Panama	SL 480 g/l	foliar	0.24-0.96		1 [c]	7
Pineapple, flower induction	Paraguay	SL 240 g/l	foliar	0.24-0.96	0.012-0.048	1 [c]	14
Pineapple, flower induction	Philippines	SL 480 g/l	foliar	0.48-0.96		1 [c]	
Pineapple, flower induction	Puerto Rico [d]	SL 480 g/l	foliar	1.12-2.24		1 [c]	2
Pineapple, flower induction	South Africa	SL 480	foliar	0.48	0.06	1 [c]	
Pineapple, flower induction	Sri Lanka	SL 480 g/l	pour in		0.012-0.024	2 [e]	M
Pineapple, flower induction	Thailand	SL 30 g/l	pour into plant		0.030-0.099	2 [f]	M

Crop	Country	Form	Application				PHI, days[1]
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Pineapple, flower induction	Thailand	SL 480 g/l	pour into plant		0.036-0.096	2 [f]	M
Pineapple, flower induction	USA	SL 480 g/l	foliar	1.12-2.24		1 [c]	2
Pineapple, flower induction	Venezuela	SL 480 g/l	foliar	0.24-0.96		1 [c]	M
Pineapple, ripening	Australia	SL 480 g/l	foliar	1.2		1 [c]	7
Pineapple, ripening	Bolivia	SL 240 g/l	foliar	0.96		1 [c]	14
Pineapple, ripening	Costa Rica	SL 480 g/l	foliar	0.6-1.2		1 [c]	7
Pineapple, ripening	Dominican Republic	SL 480 g/l	foliar	0.72-0.96		1 [c]	6
Pineapple, ripening	Ecuador	SL 480 g/l	foliar	0.60-1.2		1 [c]	M
Pineapple, ripening	El Salvador	SL 480 g/l	foliar	0.6-1.2		1 [c]	7
Pineapple, ripening	Guatemala	SL 480 g/l	foliar	0.6		1 [c]	8
Pineapple, ripening	Honduras	SL 480 g/l	foliar	0.6-1.2		1 [c]	7
Pineapple, ripening	Ivory Coast	SL 480 g/l	foliar	0.96-1.9		1 [c]	M
Pineapple, ripening	Japan	SL 100 g/l	foliar		0.03-0.05	1 [c]	M
Pineapple, ripening	Malaysia	SL 100 g/l	foliar	0.22-0.33	0.022-0.028	1 [c]	M
Pineapple, ripening	Malaysia	SL 480 g/l	foliar	0.4-0.64	0.040-0.053	1 [c]	M
Pineapple, ripening	Mexico	SL 240 g/l	foliar	0.72-1.2		1 [c]	M
Pineapple, ripening	Nicaragua	SL 480 g/l	foliar	0.60-1.2		1 [c]	8
Pineapple, ripening	Nicaragua	SL 720 g/l	foliar	1.2		1 [c]	8
Pineapple, ripening	Panama	SL 480 g/l	foliar	0.6-1.2		1 [c]	8
Pineapple, ripening	Paraguay	SL 240 g/l	foliar	0.96		1 [c]	14
Pineapple, ripening	Philippines	SL 480 g/l	foliar	0.60-1.2		1 [c]	7
Pineapple, ripening	Puerto Rico [d]	SL 480 g/l	foliar	0.56-2.24		1 [c]	2
Pineapple, ripening	South Africa	SL 480	foliar	0.96-1.9		1 [c]	7
Pineapple, ripening	Sri Lanka	SL 480 g/l	foliar		0.096	1 [e]	M
Pineapple, ripening	USA	SL 480 g/l	foliar	0.56-2.24		1 [c]	2
Pineapple, ripening	Venezuela	SL 480 g/l	foliar	0.72-1.2		1 [c]	M
Pineapple, ripening [g]	Taiwan	SL 480 g/l	foliar		0.096-0.19	1	M
Rape, winter	Germany	SL 480 g/l	foliar	0.72	0.18-0.36	1	
Rye	UK	SL	foliar	0.31-0.48		1	M
Rye, winter	Germany	SL 480 g/l	foliar	0.72	0.18-0.36	1	49
Rye, winter	Netherlands	SL 480 g/l	foliar	0.48-0.72		1	M
Tomato	Argentina	SL 480 g/l	foliar	0.96-1.9		1	20

Crop	Country	Form	Application				PHI, days[1]
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Number	
Tomato	Australia	SL 480 g/l	foliar	0.86		1	7
Tomato	Bolivia	SL 240 g/l	foliar	0.96-1.92		1	21
Tomato	Canada	SL 240 g/l	foliar	0.9-1.5		1	M
Tomato	Chile	SL 480 g/l	foliar	0.96-1.9		1	M
Tomato	Costa Rica	SL 480 g/l	foliar	0.72-0.96		1	7
Tomato	Dominican Republic	SL 720 g/l	foliar	0.72-1.1		1	6
Tomato	El Salvador	SL 480 g/l	foliar	0.72-0.96		1	7
Tomato	Guatemala	SL 480 g/l	foliar	0.72-0.96		1	8
Tomato	Honduras	SL 480 g/l	foliar	0.72-0.96		1	7
Tomato	India	SL 480 g/l	post harvest dip		0.25	1	
Tomato	Korea, South	SL 480 g/l	foliar		0.029	1	M
Tomato	Mexico	SL 240 g/l	foliar	0.96-1.92		1	M
Tomato	Mexico	SL 480 g/l	foliar	0.96-1.92		1	M
Tomato	Netherlands	SL 480 g/l	foliar		0.048		3
Tomato	Netherlands	SL 480 g/l	foliar	0.24-0.72	0.048	1 g	3
Tomato	New Zealand	SL 480 g/l	foliar	0.96-1.68	0.077-0.49	1	7
Tomato	New Zealand	SL 480 g/l	foliar		0.086	1 g[h]	7
Tomato	Nicaragua	SL 480 g/l	foliar	0.72-0.96		1	7
Tomato	Nicaragua	SL 720 g/l	foliar	0.72-1.1		1	7
Tomato	Panama	SL 480 g/l	foliar	0.72-0.96		1	7
Tomato	Paraguay	SL 240 g/l	foliar	0.96-1.9		1	21
Tomato	Spain	SL 480 g/l	foliar		0.072-0.096	1 fg	10
Tomato	Sri Lanka	SL 480 g/l	post harvest dip		0.048-0.096	1	M
Tomato	Taiwan	SL 480 g/l	foliar		0.016-0.024	1	M
Tomato	U.K. and Ireland	SL 480 g/l	foliar		0.048	1	5
Tomato	UK	SL 480 g/l	foliar		0.048	1 g	5
Tomato	Uruguay	SL 480 g/l	foliar	0.96-1.92		1	10
Tomato	Venezuela	SL 480 g/l	foliar	0.36-0.60		1	M
Tomato, processing	Greece	SL 480 g/l	foliar	1.2-1.68		1	4
Tomato, processing	Italy	SL 240 g/l	foliar	1.4-1.9		1	10
Tomato, processing	Italy	SL 480 g/l	foliar	1.4-1.9		1	10
Tomato, processing	Japan	SL 100 g/l	foliar	0.3		1	M
Tomato, processing	Portugal	SL 480 g/l	foliar	0.72-0.96		1	7
Tomato, processing	USA	SL 240 g/l	foliar	0.35-1.83 [i]		1	3
Tomato, table	Greece	SL 480 g/l	foliar		0.096-0.12	1 fg	4
Tomato, table	Italy	SL 240 g/l	foliar		0.096-0.12	1	10
Tomato, table	Italy	SL 480 g/l	foliar		0.096-0.12	1	10
Tomato, table	Japan	SL 100 g/l	foliar		0.02-0.03	1	M
Tomato, table	USA	SL 240 g/l	foliar	0.35-1.4		1	3
Triticale	Germany	SL 660 g/l	foliar	0.50	0.17-0.50	1	49
Triticale	UK	SL	foliar	0.23-0.48		1	M
Wheat, spring	UK	SL	foliar	0.23-0.36		1	M
Wheat, summer	Germany	SL 480 g/l	foliar	0.36	0.09-0.18	1	49
Wheat, summer	Netherlands	SL 480 g/l	foliar	0.24		1	M
Wheat, winter	Germany	SL 480 g/l	foliar	0.36	0.09-0.18	1	49
Wheat, winter	Netherlands	SL 480 g/l	foliar	0.36-0.48		1	M

[1]M: a specific PHI has not been set. Harvest at maturity

[a] chemical thinning of flowers at the beginning of flowering

[b] fg: approved for both field and glasshouse use.

[c] 2 applications are permitted, one for flower induction (6-10 months before harvest) and one for ripening (1-2 weeks before harvest).

[d] the USA label is followed

[e] 3 applications are permitted, 2 for flower induction at a 7-days interval (6-10 months before harvest) and one for ripening (1-2 weeks before harvest)

[f] 2 applications, 7 days apart

[g] for local consumption only, not export.

[h] g: glasshouse use

[i] use 0.35-0.91 kg ai/ha for early season varieties and 0.91-1.8 kg ai/ha for late season.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised trials on grapes, pineapples, cantaloupes, peppers and tomatoes.

in peppers when stored frozen.	Grapes. *France, USA.*
Table 3	
Table 4	Pineapples. *Ivory Coast, Brazil, Costa Rica.*
Table 5	Cantaloupes. *USA.*
	Peppers. *USA.*
Table 6	
Table 7	Tomatoes. *Belgium, Netherlands, Portugal, UK, USA.*

Where residues were not detected, they are recorded in the Tables as below the limit of determination (LOD), e.g. <0.05 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although trials included untreated control plots, control residues are recorded in the Tables only if they exceeded the LOD. Residues are recorded uncorrected for recovery. Where the residue at a longer PHI exceeds that at the GAP PHI the higher residue is taken as being derived from GAP.

Supervised trials on grapes, pineapples, cantaloupes, peppers and tomatoes were reviewed by the 1994 JMPR. Data from the relevant trials are repeated in this evaluation with slightly more detail to increase clarity. Because the data are taken from the original reports or summaries recently supplied by the manufacturer they show a few small difference from Tables 5-7 of the 1994 evaluation.

Ethephon was applied by a research knapsack sprayer in two grape trials in France in 1995. The plots consisted of 6 rows of 40 m. Field samples of 3 kg were stored in a freezer for 3 months before analysis. Wine was produced from the grapes and ethephon was determined in the must and

wine. The 1994 JMPR reported that ethephon was stable for at least 2 years in grapes when stored frozen.

Airblast sprayers were used to apply ethephon to grapes in three US trials in 1994 (plot sizes 0.024-0.030 ha). Triplicate field samples of at least 1.8 kg from each treated plot were stored in a freezer for approximately 25 weeks before analysis.

Pineapples were sprayed with CO_2 backpack sprayers in supervised trials in Costa Rica in 1998. Plots were 42.5 m^2 and field samples of 3 fruits were stored in a freezer for 71 days before analysis. The 1994 JMPR reported that ethephon was stable for at least 2 years in pineapples when stored frozen. Residues in the whole fruit were calculated from levels in the pulp and peel, which were analysed separately. Residues were generally not detected in the pineapple pulp (LOD 0.1 mg/kg). A value of 0.1 mg/kg was assumed for residues below the LOD for calculation of residues in the whole fruit.

Tractor-mounted boom sprayers and CO_2 powered backpack sprayers were used in a series of US trials on cantaloupes in 1994 where plot sizes ranged from 0.0042-0.0372 ha. Triplicate field samples of 6 fruit from each treated plot were stored in freezers for 5-8 months before analysis. The 1994 JMPR reported that ethephon was stable for at least 6 months in cantaloupes when stored frozen. In two trials (94-0362-AZ and 94-0360-TX) the samples were stored for 7-8 months, which is acceptable. Whole fruit were analysed.

Ethephon was applied to tomatoes by helicopter in 2 US trials in 1991 where plot sizes were 0.25 and 0.32 ha. A tractor-mounted boom sprayer was used in 2 other trials at the same site and a custom-designed sprayer in the fifth. Plot sizes were 0.012-0.22 ha in the trials with ground application. Triplicate field samples of 16 fruit from each treated plot were stored in freezers for 22-27 months before analysis. The 1994 JMPR reported that ethephon was stable for at least 2 years in tomatoes when stored frozen. A period of 27 months is acceptable.

Summary information was provided by the European Commission on tomato trials in Belgium, The Netherlands, Portugal and the UK, but did not include field reports, analytical validation or residues in control plots.

In a series of supervised trials on hot and sweet peppers in the USA in 1994, ethephon was applied with a variety of spray equipment: a high-clearance row crop sprayer, an offset broadcast sprayer and CO_2-pressure backpack sprayers. Plot sizes were in the range 0.0025-0.015 ha. Triplicate field samples of 1.1 kg from each treated plot were stored in freezers for 2-7 months before analysis. The 1994 JMPR reported that ethephon was stable for at least 2 years in peppers when stored frozen.

Table 3. Ethephon residues in grapes resulting from supervised trials in France (Grolleau, 1997) and USA (Lee, 1995a), and from trials reviewed by the 1994 JMPR. Analyses of replicate field samples from each trial are shown separately. Double-underlined residues are from treatments according to GAP and were used for estimation of maximum residue and STMR levels.

Country, Year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref..
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
France, 1995 (Syrah)	SL	0.45	0.45	99	1	0 25 35	0.92 0.69 mean 0.80 0.34 0.37 mean 0.35 0.52 0.23 mean <u>0.37</u>	EA950185
France, 1995 (Grenache)	SL	0.47	0.45	105	1	0 25 38	1.2 0.85 mean 1.0 0.19 0.16 mean 0.17 0.16 0.35 mean <u>0.25</u>	EA950185

Country, Year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref..
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
USA (CA), 1994 (Flame Seedless)	SL	0.56	0.122	460	1	7 10 14	0.43 0.23 0.35 mean 0.34 0.41 0.23 0.31 mean 0.32 0.37 0.17 0.19 mean 0.24	94-0378
USA (CA), 1994 (Thompson Seedless)	SL	0.56	0.12	460	1	7 10 14	0.38 0.27 0.42 mean 0.36 0.34 0.34 0.32 mean 0.33 0.37 0.35 0.27 mean 0.33	94-0379
USA (CA), 1994 (Thompson Seedless)	SL	0.56	0.080	700	1	7 10 14	0.25 0.18 0.26 mean 0.23 0.17 0.22 0.41 mean 0.27 0.13 0.20 0.19 mean 0.17	94-0380
Trials summarized by 1994 JMPR[1]								
USA (CA), 1989 (Flame Seedless)	SL	0.56		468	1	7 10 14	2.2 1.0 0.82	ref. 46 1994 JMPR 89-121
USA (CA), 1989 (Flame Seedless)	SL	0.56		468	1	7 10 14	0.07 0.07 <0.06	ref. 46 1994 JMPR 89-122
USA (CA), 1989 (Flame Seedless)	SL	0.56		468	1	7 10 14	0.53 0.42 0.35	ref. 46 1994 JMPR 89-123
USA (CA), 1989 (Thompson Seedless)	SL	0.56		468	1	45 60 75	0.15 0.10 0.08	ref. 46 1994 JMPR 89-144
USA (CA), 1989 (Thompson Seedless)	SL	0.56		468	1	45 60 75	0.21 0.31 0.15	ref. 46 1994 JMPR 89-145
USA (CA), 1978 (Thompson Seedless)		0.56			1	45	0.46	ref. 13 1994 JMPR
USA (CA), 1978 (Thompson Seedless)		0.56			1	47	0.47	ref. 13 1994 JMPR
USA (CA), 1978 (Thompson Seedless)		0.56			1	46	0.15	ref. 13 1994 JMPR
USA (CA), 1978 (Thompson Seedless)		0.56			1	45	0.24	ref. 13 1994 JMPR
USA (CA), 1978 (Thompson Seedless)		0.56			1	47	0.42	ref. 13 1994 JMPR

[1] Residues corrected for recoveries

Table 4. Ethephon residues in pineapples resulting from supervised trials in the Ivory Coast (Maestracci, 1998a), Brazil (Garcia and Carvalho, 1996) and Costa Rica (Maestracci, 1998b), and from trials reviewed by the 1994 JMPR. Analyses of replicate field samples from each trial from a treated plot or samples from replicate plots are shown separately. Double-underlined residues are from treatments according to GAP and were used for estimation of maximum residue and STMR levels.

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg [1]			Ref.
	Form	kg ai/ha	kg ai/hl	water l/ha	no.		peel	pulp	whole fruit (mean)	
Ivory Coast, 1997 (Cayenne lisse)	SL	1.4	0.048	2978	1	0 2 3 7	0.33 0.69 0.51 <0.1 0.59 0.68 0.10 0.15	<0.1 (2) <0.1 (2) <0.1 (2) <0.1 (2)	0.21 0.16 <u>0.28</u> 0.11	9816152
Brazil, 1996 (Pearl)	SL	0.96	0.24	400	1	14			<0.05 (2)	CP-2431/96
Brazil, 1996 (Pearl)	SL	1.9	0.48	400	1	14			<0.05 (2)	CP-2431/96
Costa Rica, 1998 (Del Monte Gold)	SL	1.6	0.13	1273	1	0 2 3 7	0.38 0.41 0.13 <0.1	<0.1 0.11 <0.1 <0.1	0.19 0.20 0.11 <u><0.1</u>	R&D/CRLD /AN/msa/981 6197
Costa Rica, 1998 (Del Monte Gold)	SL	1.6	0.13	1215	1	0 2 3 7	0.14 <0.1 <0.1 <0.1	<0.1 <0.1 <0.1 <0.1	0.11 <0.1 <0.1 <u><0.1</u>	R&D/CRLD /AN/msa/981 6197
Trials summarized by 1994 JMPR [2]										
USA (HI), 1990 (Smooth Cayenne)		2.2		100	2 [3]	1 2 4 8			0.22 0.12 <u>0.13</u> 0.08	ref. 61 1994 JMPR. 89-130
USA (HI), 1990 (Smooth Cayenne)		2.2		100	2 [3]	1 2 4 8			0.38 0.07 <u>0.09</u> 0.06	ref. 61 1994 JMPR. 89-131
USA (HI), 1990 (Smooth Cayenne)		2.2		100	2 [3]	2 4 8			0.41 <u>0.97</u> 0.72	ref. 61 1994 JMPR. 89-132
USA (HI), 1990 (Smooth Cayenne)		2.2		100	2 [3]	1 2 4 8			1.3 <u>0.86</u> 0.75 0.69	ref. 61 1994 JMPR. 89-133
USA (HI), 1990 (Champaka)		2.2		100	2 [3]	1 2 4 8			0.62 0.40 0.36 <u>0.76</u>	ref. 61 1994 JMPR. 89-134
USA (HI), 1990 (Champaka)		2.2		100	2 [3]	1 2 4 8			0.73 0.26 <u>0.59</u> 0.47	ref. 61 1994 JMPR. 89-135

[1] Residues in whole fruit calculated from residues in peel and pulp for trials 9816152 and 9816197. Undetectable residues (<0.1 mg/kg) were assumed to be 0.1 mg/kg in the calculation of whole fruit residues.
[2] Residues corrected for recoveries.
[3] First application for flower initiation.

Table 5. Ethephon residues in cantaloupes resulting from supervised trials in the USA (Lee, 1995b), and from trials reviewed by the 1994 JMPR. Analyses of replicate field samples from each trial are shown separately. Double-underlined residues are from treatments according to GAP and were used for estimation of maximum residue and STMR levels.

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	Water, l/ha	no.			
USA (CA), 1994 (Juan Canary)	SL	0.86	0.22	385	1	2	0.36 0.19 0.51 mean <u>0.35</u>	94-0356-CA
USA (CA), 1994 (Hales Best Jumbo)	SL	0.83	0.19	427	1	2	0.33 0.29 0.13 mean <u>0.25</u>	94-0357-CA
USA (CA), 1994 (Topmark)	SL	0.84	0.23	373	1	2	0.71 0.48 0.69 mean <u>0.63</u>	94-0358-CA
USA (CA), 1994 (Topmark)	SL	0.86	0.20	430	1	2	0.43 0.52 0.31 mean <u>0.42</u>	94-0359-CA
USA (TX), 1994 (Primos)	SL	0.84	0.20	420	1	2	0.36 0.30 0.28 mean <u>0.31</u>	94-0360-TX
USA (TX), 1994 (TAX UVALDE)	SL	0.84	0.22	375	1	2	0.15 0.18 0.22 mean <u>0.18</u>	94-0361-TX
USA (AZ), 1994 (Topmark)	SL	0.84	0.18	463	1	2	0.34 0.72 0.57 mean <u>0.54</u>	94-0362-AZ
Trials summarized by 1994 JMPR								
USA (TX), 1972 (Perlite)		0.90			1	0 2 5	0.07 0.06 <u>0.07</u>	ref. 10 1994 JMPR
USA (CA), 1969 (Topmark)		0.96			1	3	<u>0.18</u>	ref. 10 1994 JMPR
USA (CA), 1969 (Topmark)		0.90			1	3 5	<u>0.16</u> 0.08	ref. 10 1994 JMPR
USA (CA), 1970 (PMR 45)		0.90			1	3	<u>0.30</u>	ref. 10 1994 JMPR
USA (CA), 1969 (Topmark)		0.90			1	4	<u>0.15</u>	ref. 10 1994 JMPR
USA (CA), 1970 (PMR 45)		0.90			1	4	<u>0.23</u>	ref. 10 1994 JMPR
USA (CA), 1969 (PMR 45)		0.90			1	5	<u>0.23</u>	ref. 10 1994 JMPR

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	Water, l/ha	no.			
USA (TX), 1989 (Mainstream)	SL	0.98		54.2	1 ✈	2 4 6	0.11 0.07 0.04	ref. 41 1994 JMPR 89-126
USA (TX), 1989 (Mainstream)	SL	0.98		369	1	2 4 6	0.44 0.40 0.06	ref. 41 1994 JMPR 89-126

Table 6. Ethephon residues in peppers resulting from supervised trials in the USA (Lee and Chism, 1995), and from trials reviewed by the 1994 JMPR. Analyses of replicate field samples from each trial are shown separately. Double-underlined residues are from treatments according to GAP and were used for estimation of maximum residue and STMR levels.

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Hot peppers: USA (CA), 1994 (Jalepeno)	SL	1.1	0.24	467	1	5	0.78 0.77 0.73 mean 0.76	94-0363
Sweet peppers: USA (CA), 1994 (Giant Emperor)	SL	1.1	0.24	467	1	5	0.72 0.42 0.59 mean 0.58	94-0364
Sweet peppers: USA (TX), 1994 (Pip)	SL	1.2	0.28	421	1	5	1.3 1.8 1.1 mean 1.4	94-0365
Hot peppers: USA (TX), 1994 (TAM Mild Jalapeno)	SL	1.1	0.27	402	1	4	2.0 1.8 1.6 mean 1.8	94-0366
Sweet peppers: USA (NC), 1994 (California Wonder)	SL	1.1	0.30	374	1	5	1.7 2.6 1.9 mean 2.1	94-0367
Hot peppers: USA (AZ), 1994 (AZ 10 Anaheim peppers)	SL	1.0	0.24	467	1	5	1.0 0.91 0.94 mean 0.96	94-0368
Hot peppers: USA (NM), 1994 (Early Jaleperno)	SL	1.1	0.28	402	1	5	0.38 0.60 0.59 mean 0.52	94-0369
Hot peppers: USA (NM), 1994 (Sonora)	SL	1.1	0.29	402	1	5	2.7 2.1 2.3 mean 2.4	94-0370
Sweet peppers: USA (FL), 1994 (Boynton Belle)	SL	1.1	0.093	1178	1	5	1.04 0.88 1.07 mean 1.0	94-0371
Sweet peppers: USA (FL), 1994 (Jupiter)	SL	1.1	0.24	467	1	5	0.12 0.20 0.16 mean 0.16	94-0372

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Trials summarized by 1994 JMPR [1]								
USA (IA), 1973 (Large Cherry)		1.1			1	8	10.8	ref. 8 JMPR 1994
USA (IA), 1973 (Large Cherry)		1.1			1	7	9.7	ref. 8 JMPR 1994
USA (IA), 1973 (Red Cayenne)		1.1			1	8	22.3	ref. 8 JMPR 1994
USA (IA), 1973 (Red Cayenne)		1.1			1	7	26.2	ref. 8 JMPR 1994
USA (IA), 1973 (Merrimack Wonder)		1.1			1	8	8.9	ref. 8 JMPR 1994
USA (IA), 1973 (Merrimack Wonder)		1.1			1	7	6.8	ref. 8 JMPR 1994
USA (IA), 1973 (Early Pimento)		1.1			1	8	4.5	ref. 8 JMPR 1994
USA (IA), 1973 (Early Pimento)		1.1			1	7	4.3	ref. 8 JMPR 1994
USA (PA), 1973 (Large Cherry)		1.1			1	5	3.5	ref. 8 JMPR 1994
USA (PA), 1973 (Long Red Cayenne)		1.1			1	5	10.6	ref. 8 JMPR 1994
USA (PA), 1973 (Early Pimento)		1.1			1	5	5.7	ref. 8 JMPR 1994
USA (PA), 1973 (Merrimack Wonder)		1.1			1	5	7.3	ref. 8 JMPR 1994

[1] Residues corrected for recoveries.

Table 7. Ethephon residues in tomatoes resulting from supervised trials in the USA (Nygren, 1995) and Europe, and from trials reviewed by the 1994 JMPR. Analyses of replicate field samples from each trial are shown separately. Double-underlined residues are from treatments according to GAP and were used for estimation of maximum residue and STMR levels.

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Belgium, 1971	SL		0.048		1 g	0 3 9	0.19 0.07 0.17	EC summary
Belgium, 1971	SL		0.096		1 g	0 3 9	1.1 1.6 0.85	EC summary

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
Belgium, 1972 (Hollandia's Special)	SL		0.054		1 g	6 10 14 17 21	1.3 0.60 1.7 1.2 0.32	EC summary
Belgium, 1972 (Hollandia's Special)	SL		0.072		1 g	6 10 14 17 21	2.3 2.3 1.1 1.8 0.31	EC summary
Belgium, 1972 (Hollandia's Special)	SL		0.090		1 g	6 10 14 17 21	2.1 2.1 1.7 0.86 1.0	EC summary
Belgium, 1972 (Hollandia's Special)	SL		0.11		1 g	6 10 14 17 21	1.9 1.2 1.1 1.4 0.93	EC summary
Netherlands, 1976		1.2		2500	1 g	3 7	1.6 1.3 1.4 1.1 mean 1.4 1.5 1.5 1.0 1.1 mean 1.3	EC summary
Netherlands, 1976 (Extase)		1.2		2500	1 g	3 7	1.5 1.7 1.5 1.2 mean 1.5 1.5 1.6 1.7 1.4 mean 1.6	EC summary
Netherlands, 1985 (Turbo)	sludge	brushing of stems with sludge + water at 240 g ai/l			1 g	3 6 12	2.9 1.8 3.4 4.2 mean 3.1 3.4 3.8 5.1 5.4 mean 4.4 3.2 4.8 7.7 3.4 mean 4.8	EC summary
Netherlands, 1985 (Abunda)	sludge	brushing of stems with sludge + water at 240 g ai/l			1 g	3 6 12	2.7 1.9 2.9 3.2 mean 2.7 4.6 4.1 3.2 6.2 mean 4.5 5.1 3.9 4.4 6.1 mean 4.9	EC summary
Portugal	SL	0.92			1	1 6 9 12 15 18	0.01 0.10 0.08 0.08 0.03 0.03	EC summary
Portugal	SL	1.85			1	1 6 9 12 15 18	0.02 0.14 0.12 0.12 0.06 0.03	EC summary
UK (Guernsey), 1980 (Sarina)	SL		0.048		1 g	3 3 3 4 4 4	2.7 2.6 2.6 2.6 2.4 2.2 2.1 2.3 2.2 3.1 3.2 3.2 mean 2.6 2.0 2.1 2.4 2.3 1.9 2.1 1.8 2.1 2.1 2.3 1.8 1.4 mean 2.0	EC summary

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
USA (CA), 1991 (Ace)	SL	1.7	0.53	326	1	3 7 14	1.6 2.2 1.1 mean 1.7 0.51 1.2 1.2 mean 0.97 0.78 0.66 0.44 mean 0.63	91-307
USA (CA), 1991 (Ace)	SL	1.8	1.3	134	1 ✈	3 7 11	1.1 1.3 1.4 mean 1.2 0.93 0.66 0.83 mean 0.81 0.29 0.44 0.39 mean 0.37	91-308
USA (CA), 1991 (Ace)	SL	1.8	0.53	341	1	3 7 14	0.48 0.61 mean 0.55 0.43 0.25 0.36 mean 0.35 0.22 0.12 0.12 mean 0.15	91-309
USA (CA), 1991 (Ace)	SL	1.7	1.3	131	1 ✈	3 7 11	0.69 0.69 0.49 mean 0.62 0.75 0.40 0.89 mean 0.68 0.40 0.34 1.3 mean 0.67	91-310
USA (FL), 1991 (BHN)	SL	1.8	0.38	471	1	3 3 7 7 10 10	0.17 0.36 0.37 mean 0.30 c 0.01 0.12 0.07 0.04 mean 0.08 c 0.02 0.06 0.05 0.04 mean 0.05 c 0.02	91-311
Trials summarized by 1994 JMPR [1]								
USA (CA), 1989 (UC-82)	SL	1.8		76	1 ✈	0 3 7	0.18 0.10 0.09	ref. 47 1994 JMPR. 89-119
USA (CA), 1989 (UC-82)	SL	2.1		204	1	0 3 7	0.48 0.44 0.27	ref. 47 1994 JMPR. 89-120
USA (CA), 1989 (Sun Seed 5715)	SL	1.8		93	1 ✈	3 7 14	0.66 0.92 0.69	ref. 47 1994 JMPR 89-136
USA (CA), 1989 (Sun Seed 5715)	SL	2.0		206	1	3 7 14	0.02 <0.02 0.15	ref. 47 1994 JMPR 89-137
USA (FL), 1990 (Sunny)	SL	1.8		187	1	3 7 14	<0.02 <0.02 <0.02	ref. 64 1994 JMPR 90-492
USA (FL), 1990 (Sunny)	SL	1.8		93	1 ✈	3 7 14	0.32 0.05 0.06	ref. 64 1994 JMPR 90-493
USA (PA), 1970 (Campbell 29)		1.8			1	6 15 21	1.41 0.40 0.41	ref. 71 1994 JMPR
USA (CA), 1970 (VF-145-B7879)		1.8			1	14	0.21	ref. 71 1994 JMPR

Country, year (variety)	Application					PHI, days	Ethephon, mg/kg	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.			
USA (CA), 1970 (VF-145-B7879)		1.9			1	1 6 9 12 15 21	0.02 0.14 0.12 0.10 0.06 0.12	ref. 71 1994 JMPR
USA (CA), 1970 (Pakmor)		1.9			1	1 3	0.07 0.23	ref. 71 1994 JMPR
USA (CA), 1970 (Calmart)		1.9			1	1 3	0.11 0.37	ref. 71 1994 JMPR
USA (CO), 1970 (Mech 9)		1.8			1	15	0.50	ref. 71 1994 JMPR
USA (MD), 1970 (Roma)		1.8			1	14	1.14	ref. 71 1994 JMPR

✈ aerial application
c: control
g: glasshouse
[1] residues corrected for recoveries

Table 8. Interpretation table for ethephon residues in grapes, pineapples, peppers, tomatoes and cantaloupes. GAP and trial conditions are compared for treatments considered valid for the estimation of maximum residue levels and STMRs.

Crop	Country	Use pattern				Trial	Ethephon, mg/kg
		kg ai/ha	kg ai/hl	No of appl	PHI days[1]		
Grapes							
GAP	USA	0.56		1	14		
trial	USA	0.56		1	14	94-0378	0.24
trial	USA	0.56		1	14	94-0379	0.33
trial	USA	0.56		1	14	94-0380	0.17
trial	USA	0.56		1	45	ref. 13 JMPR 1994	0.46
trial	USA	0.56		1	47	ref. 13 JMPR 1994	0.47
trial	USA	0.56		1	46	ref. 13 JMPR 1994	0.15
trial	USA	0.56		1	45	ref. 13 JMPR 1994	0.24
trial	USA	0.56		1	47	ref. 13 JMPR 1994	0.42
trial	USA	0.56		1	14	ref. 46 JMPR 1994 [2]	0.82
trial	USA	0.56		1	14	ref. 46 JMPR 1994 [2]	<0.06
trial	USA	0.56		1	14	ref. 46 JMPR 1994 [2]	0.35
trial	USA	0.56		1	45	ref. 46 JMPR 1994 [2]	0.15
trial	USA	0.56		1	60 (45)	ref. 46 JMPR 1994 [2]	0.31
GAP	France	0.45		1			
trial	France	0.47		1	35 (25)	EA950185	0.37
trial	France	0.47		1	38 (25)	EA950185	0.25
Pineapples							
GAP	Bolivia	0.96		1	14		
trial	Brazil	0.96		1	14	CP-2431/96	<0.05
trial	Brazil	1.9		1	14	CP-2431/96	<0.05

Crop	Country	Use pattern				Trial	Ethephon, mg/kg
		kg ai/ha	kg ai/hl	No of appl	PHI days[1]		
GAP	Costa Rica	1.2		1	7		
trial	Costa Rica	1.6		1	7	R&D/CRLD/AN/msa/9816197	<0.1
trial	Costa Rica	1.6		1	7	R&D/CRLD/AN/msa/9816197	<0.1
GAP	Ivory Coast	1.9		1			
trial	Ivory Coast	1.4		1	3	9816152	0.28
GAP	USA	2.2		1	2		
trial	USA	2.2		2	4 (2)	ref. 61 JMPR 1994	0.13
trial	USA	2.2		2	4 (2)	ref. 61 JMPR 1994	0.09
trial	USA	2.2		1	4 (2)	ref. 61 JMPR 1994	0.97
trial	USA	2.2		2	2	ref. 61 JMPR 1994	0.86
trial	USA	2.2		2	8 (2)	ref. 61 JMPR 1994	0.76
trial	USA	2.2		2	4 (2)	ref. 61 JMPR 1994	0.59
Cantaloupes							
GAP	USA	0.84		1	2		
trial	USA	0.86		1	2	94-0356-CA	0.35
trial	USA	0.83		1	2	94-0357-CA	0.25
trial	USA	0.84		1	2	94-0358-CA	0.63
trial	USA	0.86		1	2	94-0359-CA	0.42
trial	USA	0.84		1	2	94-0360-TX	0.31
trial	USA	0.84		1	2	94-0361-TX	0.18
trial	USA	0.84		1	2	94-0362-AZ	0.54
trial	USA	0.90		1	3	ref. 10 JMPR1994	0.16
trial	USA	0.90		1	3	ref. 10 JMPR1994	0.30
trial	USA	0.90		1	4	ref. 10 JMPR1994	0.15
trial	USA	0.96		1	3	ref. 10 JMPR1994	0.18
trial	USA	0.90		1	4	ref. 10 JMPR1994 [3]	0.23
trial	USA	0.90		1	5	ref. 10 JMPR1994 [3]	0.23
trial	USA	0.90		1	5 (2)	ref. 10 JMPR1994	0.07
trial	USA	0.98		1	2	ref. 41 JMPR1994	0.11
trial	USA	0.98		1	2	ref. 41 JMPR1994	0.44
Peppers							
GAP	USA	1.1		1	5		
trial	USA	1.1		1	5	94-0363	0.76
trial	USA	1.1		1	5	94-0364	0.58
trial	USA	1.2		1	5	94-0365	1.4
trial	USA	1.1		1	4	94-0366	1.8
trial	USA	1.1		1	5	94-0367	2.1
trial	USA	1.0		1	5	94-0368	0.96
trial	USA	1.1		1	5	94-0369	0.52
trial	USA	1.1		1	5	94-0370	2.4
trial	USA	1.1		1	5	94-0371	1.0
trial	USA	1.1		1	5	94-0372	0.16
trial	USA	1.12		1	8	ref. 8 JMPR 1994	10.8
trial	USA	1.12		1	7	ref. 8 JMPR 1994	9.7
trial	USA	1.12		1	8	ref. 8 JMPR 1994	22.3
trial	USA	1.12		1	7	ref. 8 JMPR 1994	26.2
trial	USA	1.12		1	8	ref. 8 JMPR 1994	8.9
trial	USA	1.12		1	7	ref. 8 JMPR 1994	6.8
trial	USA	1.12		1	8	ref. 8 JMPR 1994	4.5
trial	USA	1.12		1	7	ref. 8 JMPR 1994	4.3

Crop	Country	Use pattern				Trial	Ethephon, mg/kg
		kg ai/ha	kg ai/hl	No of appl	PHI days[1]		
trial	USA	1.12		1	5	ref. 8 JMPR 1994	3.5
trial	USA	1.12		1	5	ref. 8 JMPR 1994	10.6
trial	USA	1.12		1	5	ref. 8 JMPR 1994	5.7
trial	USA	1.12		1	5	ref. 8 JMPR 1994	7.3
Tomatoes							
GAP	USA	1.83		1	3		
trial	USA	1.7		1	3	91-307	1.7
trial	USA	1.8		1	3	91-308	1.24
trial	USA	1.8		1	3	91-309	0.55
trial	USA	1.7		1	7 (3)	91-310	0.68
trial	USA	1.8		1	3	91-311	0.30
trial	USA	1.75		1	3	ref. 47 JMPR 1994	0.10
trial	USA	2.13		1	3	ref. 47 JMPR 1994	0.44
trial	USA	1.79		1	7 (3)	ref. 47 JMPR 1994	0.92
trial	USA	2.00		1	14 (3)	ref. 47 JMPR 1994	0.15
trial	USA	1.8		1	3	ref. 64 JMPR 1994	<0.02
trial	USA	1.8		1	3	ref. 64 JMPR 1994	0.32
trial	USA	1.8		1	6	ref. 71 JMPR 1994 [4]	1.41
trial	USA	1.9		1	6	ref. 71 JMPR 1994 [4]	0.14
trial	USA	1.9		1	3	ref. 71 JMPR 1994 [4]	0.23
trial	USA	1.9		1	3	ref. 71 JMPR 1994 [4]	0.37
trial	USA	1.8		1	14	ref. 71 JMPR 1994 [4]	1.14
trial	USA	1.8		1	14	ref. 71 JMPR 1994 [4]	0.21
trial	USA	1.8		1	15	ref. 71 JMPR 1994 [4]	0.50

[1] A shorter PHI in parentheses is the GAP PHI, but the residue was higher at the longer PHI and was used for the evaluation
[2] Ref. 44 is also given in Table 5 of the 1994 residue evaluations, but it does not refer to grapes
[3] In Table 8 (page 523) of the 1994 JMPR residue evaluations these appear to be different PHIs in the same trial, but they were at different places and times (1969 and 1970).
[4] Shown as ref. 12 in 1994 JMPR Evaluations, but should be ref. 71.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

The Meeting received information on the fate of ethephon residues during vinification.

Grolleau (1997) treated Syrah and Grenache grapes with ethephon in trials in France and harvested the grapes 5 weeks after treatment for the production of red wine. Approximately 40 kg of grapes were crushed with an electric crusher/stemmer and potassium metabisulfite was added. Dry active yeast was added to the must and the progress of the fermentation was followed by measuring the density, temperature and pH of the must. In the Syrah trial 34 g/l of white sugar was added to the must during fermentation, increasing the probable alcoholic content by 2%. When fermentation was complete the solids were pressed to obtain the maximum quantity of wine. The wine in a completely filled demijohn, after malolactic fermentation, was treated with potassium metabisulfite and allowed to stand for clarification. The wine was then decanted into another demijohn, treated with gelatin to improve clarification, then sulfited and allowed to stand for at least 15 days. The wine was finally filtered under nitrogen pressure and bottled. Bottles of wine were immediately stored frozen (-20°C) pending analysis. The residues in the grapes, must and wine are shown in Table 9.

Table 9. Ethephon residues in grapes, must and wine resulting from supervised trials on grapes (Table 3) and subsequent vinification, France 1995 (Grolleau, 1997).

Variety	Rate, kg ai/ha	PHI, days	Wt. processed	Ethephon, mg/kg			Ref.
				Grapes	Must	Wine at bottling	
Syrah	0.45	35	40 kg	0.37	0.34	0.77	EA950185
Grenache	0.47	38	40 kg	0.25	0.17	0.36	EA950185

The 1994 JMPR evaluated processing trials on a number of commodities including grapes, pineapples and tomatoes.

Processing factors for raisins were 0.92, 1.0, 1.4 and 3.2 (Table 5, p. 519 of residue evaluations) and 4.5 and 5.3 (p. 548) giving a mean processing factor of 2.7.

Processing factors for pineapple products calculated from data in Table 25 of the residue evaluations, p. 549, were canned slices 0.28, canned juice 0.39, 'ion exchange' juice 0.15.

Processing factors for tomato products calculated from data in Table 26 of the residue evaluations, p. 550, were canned fresh juice 0.34, canned purée 0.60, canned paste 0.75.

Residues in the edible portion of food commodities

A processing study on Syrah and Grenache grapes gave processing factors for wine of 2.08 and 1.44 respectively, mean 1.76.

Limited information was available from supervised trials in the Ivory Coast and Costa Rica on the distribution of ethephon residues in pineapples (Table 4). In the Ivory Coast trial residues in 4 samples of pulp were below the LOD (0.1 mg/kg) while the residues in the corresponding samples of peel were 0.51, 0.31, 0.64 and 0.13 mg/kg. In the Costa Rica trials a residue of 0.11 mg/kg in the pulp corresponded to 0.41 mg/kg in the peel. In 3 other samples the residues were below the LOD (0.1 mg/kg) in the pulp and 0.38, 0.13 and 0.14 mg/kg in the peel. The mean ratio of pulp to whole fruit residues was <0.66 (range <0.36 to <0.91, n = 8). All the calculated ratios except one involve denominators below the LOD and are therefore exaggerated. However, the distribution between peel and pulp may depend on the interval between treatment and harvest, particularly in the first days after treatment, and the calculated distribution factor should be used cautiously.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Meeting received information from The Netherlands on ethephon residues in food in commerce during 1997-1998. The residues were below the LOD (0.3 mg/kg) in all samples analysed: apples 45 samples, pears 9, cherries 20, currants 20, onions 10, tomatoes 14 and sweet peppers 9.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware of the following national MRLs.

Country	MRL, mg/kg	Commodity
Argentina	2	peppers, tomato
Australia	2	pineapple, tomato
Australia	10	grapes
Brazil	0.5	pineapple
Brazil	1.5	tomato
Canada	2	tomato
France	0.05	grapes
India	2	pineapple, tomato
Ireland	3	peppers, tomato
Italy	0.05	wine grapes
Italy	1	wine and grape juice
Italy	3	table grapes, tomato
Japan	T 2	grapes, pineapple
Japan	T 3	tomato
Korea, South	1	pineapple
Korea, South	2	grapes
Korea, South	3	tomato
Netherlands	3	peppers, tomato
New Zealand	1	tomato
Poland	0.05	berry fruits except currants, vegetables except as otherwise listed
Poland	3	tomato
Poland	5	currants, black, red, white
Portugal	3	peppers, tomato
South Africa	1	pineapple
South Africa	5	grapes
Taiwan	2	grapes, pineapple, tomato
UK	3	peppers, tomato
USA	2	cantaloupe, grapes, pineapple, tomato
USA	3	pineapple fodder and forage
USA	30	peppers
USA	65	raisin waste

APPRAISAL

Ethephon was evaluated in the CCPR Periodic Review Programme by the 1994 JMPR. Recommended MRLs for cantaloupe, grapes, peppers, pineapple and tomato were retained at Step 7B by the 31st Session of the CCPR (1999) pending a review of new data by the 1999 JMPR.

The Meeting received information on analytical methods and GAP together with supplementary residue data on cantaloupes, grapes, peppers, pineapples and tomatoes.

A GLC analytical method involving derivatization to dimethyl ethephon with diazomethane has been used for many years and was reviewed by the 1994 JMPR. Another method depending upon the release of ethylene and its determination by headspace GLC has been developed to avoid the use of diazomethane. The LOD for fruits and vegetables is generally about 0.02 mg/kg. The method was validated for many commodities including tomatoes, pineapples, cantaloupes, peppers and grapes.

The current definition of the residue is ethephon. The Meeting agreed that this was a suitable definition for compliance with MRLs and for the estimation of dietary intake.

Ethephon is a systemic plant growth regulator, and when used on crops near maturity induces fruit ripening. It is generally inappropriate to set minimum pre-harvest intervals; it is preferable to harvest the crop at the proper stage of maturity. When a pre-harvest interval is specified it is normally shorter than necessary to avoid over-ripening.

The 1994 JMPR noted that ethephon residues were stable in the treated crops and that the PHI usually had little influence on the residue levels. Summary reports of two trials in The Netherlands in which ethephon was applied to the stems of tomato plants demonstrated rapid translocation and build-up in the fruits over 3-12 days.

The application rate (kg ai/ha) rather than the spray concentration is the prime determinant of GAP.

Supervised trials

Grapes. In France, ethephon may be used on grapes at 0.36-0.45 kg ai/ha. The residues in grapes harvested 35 and 38 days after treatment in two trials were 0.37 and 0.25 mg/kg. In both trials the levels in grapes harvested at the longer intervals were slightly higher than in fruit harvested 25 days after treatment.

Ethephon may be used at 0.56 kg ai/ha on grapes in the USA and harvesting is permitted 14 days later. The residues in grapes from three trials meeting these conditions were 0.17, 0.24 and 0.33 mg/kg.

Ethephon residues in grapes from 10 trials in the USA recorded in the 1994 JMPR Evaluations were <0.06, 0.15, 0.15, 0.24, 0.31, 0.35, 0.42, 0.46, 0.47 and 0.82 mg/kg, 14-47 days after treatment at 0.56 kg ai/ha.

The residues in grapes from the 2 French and 13 US trials according to GAP in rank order (median underlined) were <0.06, 0.15, 0.15, 0.17, 0.24, 0.24, 0.25, 0.31, 0.33, 0.35, 0.37, 0.42, 0.46, 0.47 and 0.82 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.31 mg/kg for ethephon in grapes. The maximum residue level supports the previous recommendation.

The processing factor for raisins (2.7) was applied to the estimated maximum residue level for grapes to produce an estimated maximum residue level, after rounding, for ethephon in dried grapes of 5 mg/kg. The same processing factor applied to the STMR (0.31 mg/kg) and HR (0.82 mg/kg) for grapes gave an STMR of 0.84 mg/kg and an HR-P of 2.2 mg/kg for dried grapes.

he processing factor for wine (1.76) was considered unrealistic. At the highest estimate, residues in wine should not exceed those in the grapes. The Meeting concluded that the STMR for wine should be the same as for grapes, 0.31 mg/kg.

Pineapples. Pineapples may be treated with ethephon at 1.2 kg ai/ha to induce ripening in Costa Rica, where residues were below the LOD (0.1 mg/kg) in pineapples harvested 7 days after treatment with 1.6 kg ai/ha in two trials.

The approved application rate on pineapples in the Ivory Coast is 1.9 kg ai/ha. The residue in pineapples treated at 1.4 kg ai/ha and harvested 3 days later was 0.28 mg/kg, and that in the pulp was below the LOD (0.1 mg/kg).

In Bolivia the approved treatment rate for pineapple ripening is 0.96 kg ai/ha with a PHI of 14 days. The residues in the pineapples were below the LOD (0.05 mg/kg) in 2 trials in Brazil, a neighbouring country, where the application rates were 0.96 and 1.9 kg ai/ha with harvest 14 days after treatment.

US trials were reported by the 1994 JMPR. The residues from 6 trials where the application rate was 2.2 kg ai/ha (the maximum GAP rate) were 0.09, 0.13, 0.59, 0.76, 0.86 and 0.97 mg/kg.

The US delegation to the CCPR drew attention to differences in interpretation of the data between the JMPR and the USA. For example, the USA adjusted the residue data for analytical recoveries, which converted one of the levels to 1.3 mg/kg, suggesting an MRL of 2 mg/kg. Generally, the JMPR practice is to use uncorrected results and to regard recoveries as a criterion of acceptability. The USA also drew attention to a residue of 1.1 mg/kg resulting from the low application rate of 0.56 kg ai/ha. However, it was a 1970 trial and its validity is uncertain; it seems inconsistent with the modern data and was disregarded by the 1994 JMPR. The Meeting noted the rationale for the different procedures, but agreed that the 1994 interpretations were consistent with usual JMPR practice.

Residues in pineapples from the 2 Costa Rica, 1 Ivory Coast, 2 Brazilian and 6 US trials according to GAP in rank order (median underlined) were <0.05, <0.05, 0.09, <0.1, <0.1, 0.13, 0.28, 0.59, 0.76, 0.86 and 0.97 mg/kg.

The Meeting noted that the highest residues were very close to 1 mg/kg and that residues above 1 mg/kg would be possible, and estimated a maximum residue level of 2 mg/kg and an STMR of 0.13 mg/kg for ethephon in pineapples. The maximum residue level is recommended to replace the draft MRL of 1 mg/kg.

The processing factors for juice (0.39) and canned slices (0.28) were applied to the STMR of 0.13 mg/kg to produce STMRs for ethephon in pineapple juice and canned pineapple of 0.051 and 0.036 mg/kg respectively. An HR-P of 0.27 mg/kg was estimated for canned pineapple from the highest residue in the trials of 0.97 mg/kg and the processing factor of 0.28.

Cantaloupes. US GAP permits the use of ethephon on cantaloupes at 0.84 kg ai/ha with a PHI of 2 days. In 7 US trials in 1994 according to GAP ethephon residues were 0.18, 0.25, 0.31, 0.35, 0.42, 0.54 and 0.63 mg/kg.

The 1994 JMPR evaluation reported residues in cantaloupes in 9 trials in 1969-72 and 1989 with application rates of 0.90-0.98 kg ai/ha and PHIs of 2-4 days, essentially according to current GAP, of 0.07, 0.11, 0.15, 0.16, 0.18, 0.23, 0.23, 0.30 and 0.44 mg/kg.

The residues in cantaloupes from the 16 US trials according to GAP in rank order (median underlined) were 0.07, 0.11, 0.15, 0.16, 0.18, 0.18, 0.23, 0.23, 0.25, 0.30, 0.31, 0.35, 0.42, 0.44, 0.54 and 0.63 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.24 mg/kg for ethephon in cantaloupes. The maximum residue level supports the previous recommendation.

Peppers. Ethephon is registered for use on peppers in the USA at 0.35-1.1 kg ai/ha with a 5 days PHI. In a series of 10 US trials in 1994 on sweet and hot peppers according to maximum US GAP the residues in rank order (median underlined) were 0.16, 0.52, 0.58, 0.76, 0.96, 1.0, 1.4, 1.8, 2.1 and 2.4 mg/kg.

The 1994 JMPR reviewed results from 12 US trials on peppers in 1973 where ethephon was applied at 1.12 kg ai/ha with harvest 5-8 days later, which is equivalent to current GAP. The residues in rank order (median underlined) were 3.5, 4.3, 4.5, 5.7, 6.8, 7.3, 8.9, 9.7, 10.6, 10.8, 22.3 and 26.2 mg/kg.

Clearly the two residue populations are different although the use pattern is the same; if the residues were from one population the probability of no overlap between the two sets of results would be very low. There is no explanation for the difference in terms of different analytical methods or agricultural practices. There is no direct reason to discard the 1973 data but the Meeting decided to accept the more recent results because the trials were situated in those States of the USA with major production of peppers, had better documentation, and perhaps better reflected current formulations and application equipment.

The Meeting estimated a maximum residue level of 5 mg/kg and an STMR of 0.98 mg/kg for ethephon in peppers. The maximum residue level is recommended to replace the draft MRL of 30 mg/kg.

Tomatoes. Ethephon is registered in the USA for application to tomatoes at 1.8 kg ai/ha with harvest no sooner than 3 days later. The residues in 5 US trials in 1991 according to GAP were 0.30, 0.55, 0.68, 1.2 and 1.7 mg/kg.

The 1994 JMPR reviewed 13 US residue trials in 1970-1990 where ethephon was applied at 1.75-2.1 kg ai/ha with PHIs of 3-16 days. The residues were <0.02, 0.10, 0.14, 0.15, 0.21, 0.23, 0.32, 0.37, 0.44, 0.50, 0.92, 1.14 and 1.41 mg/kg.

The Meeting received summary reports of trials on tomatoes in Europe: 6 in Belgium (1971, 1972), 4 in The Netherlands (1976, 1985), 2 in Portugal and 1 in the UK (1980). The trials were not evaluated because no field reports, analytical validation or residues from untreated control plots were available.

The residues in the 18 US trials according to GAP in rank order (median underlined) were <0.02, 0.10, 0.14, 0.15, 0.21, 0.23, 0.3, 0.32, 0.37, 0.44, 0.5, 0.55, 0.68, 0.92, 1.14, 1.2, 1.41 and 1.7mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.41 mg/kg for ethephon in tomatoes. The maximum residue level supports the previous recommendation.

The processing factors for juice (0.34) and paste (0.75) were applied to the estimated STMR for tomatoes to produce STMRs for ethephon in tomato juice and paste of 0.14 and 0.31 mg/kg respectively.

Processing. A processing study on Syrah and Grenache grapes showed higher residues in wine than in the grapes: the calculated processing factors were 2.08 and 1.44 respectively, mean 1.76, which appeared somewhat unrealistic.

The following processing factors for products from grapes, pineapples and tomatoes were derived from processing information evaluated by the 1994 JMPR: raisins 2.7, canned pineapple juice 0.39, canned pineapple slices 0.28, tomato juice 0.34, tomato paste 0.75.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels and STMRs shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue (for compliance with MRLs and for estimation of dietary intake): ethephon.

Commodity		MRL, mg/kg		STMR, mg/kg	HR or HR-P[1], mg/kg
CCN	Name	New	Previous		
VC 4199	Cantaloupe	1	1	0.24 [2]	0.63 [2]
DF 0269	Dried grapes (currants, raisins and sultanas)	5		0.84	2.2
FB 0269	Grapes	1	1	0.31	0.82
VO 0051	Peppers	5	30	0.98	2.4
FI 0353	Pineapple	2	1	0.13	0.97
	Pineapple canned			0.036	0.27
JF 0341	Pineapple juice			0.051	
VO 0448	Tomato	2	2	0.41	1.7
JF 0448	Tomato juice			0.14	
	Tomato paste			0.31	
	Wine			0.31	

[1]HR: highest residue (edible portion) from supervised trials. HR-P: highest residue in processed commodity, calculated from the HR of the raw agricultural commodity and the processing factor.
[2]Cantaloupe: STMR and HR expressed on whole fruit, not edible portion.

FURTHER WORK OR INFORMATION

Desirable

Information on the fate of ethephon during the processing of grapes to wine. The available studies suggested that ethephon was concentrated in the wine by factors of 1.4 and 2.1.

DIETARY RISK ASSESSMENT

Chronic intake

Maximum residue levels have been estimated for ethephon in canteloupes, dried grapes, peppers, pineapples and tomatoes to confirm or replace existing draft MRLs. STMRs have been estimated for the main commodities and some processed commodities. All the other values (16) used for the intake estimation are previously established CXLs. The dietary intakes of ethephon are shown in Annex III.

Estimated dietary intakes of ethephon for the 5 GEMS/Food regional diets were in the range of 2-20% of the ADI. The Meeting concluded that the intake of residues of ethephon resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The international estimate of short-term intake (IESTI) for ethephon was calculated for commodities for which MRLs were recommended and STMRs estimated and for which consumption data (large portion consumption, unit weight) were available. The results are shown in Annex IV. The IESTI ranged from 0.005 to 0.031 mg/kg bw in the total population and from 0 to 0.099 mg/kg bw in children. As no acute reference dose has been established, the acute risk assessment for ethephon was not finalized.

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ETHOXYQUIN (035)

EXPLANATION

Ethoxyquin, an antioxidant preservative, was first evaluated in 1969. It was originally identified by the 1990 CCPR as a candidate for re-evaluation (ALINORM 91/24, Appendix V). It was scheduled by the 1994 CCPR for re-evaluation by the 1994 JMPR (ALINORM 91/24A, Appendix VI, Annex 1), but removed from the 1994 JMPR schedule at the 1994 CCPR because the Committee was informed that the manufacturer was not supporting the existing CXLs for apples and pears. The US and UK delegations indicated that data might be supplied. The CCPR recommended deletion of the existing CXLs if no information became available by the 1995 Session (ALINORM 95/24, para 104).

At the 1995 CCPR, the delegation of the USA opposed deletion of the CXLs and informed the Committee that residue data on pears and a full toxicological data package would be available for the JMPR in 1996. Ethoxyquin was, therefore, scheduled for toxicological and residue reviews by the JMPR in 1998 and 1999 respectively. It was decided to postpone the withdrawal of the CXL for pear until the 28th session of the CCPR (ALINORM 95/24A, paragraph 89). The CCPR in 1996 and 1997 postponed discussion on deletion of the CXL for pear (ALINORM 97/24, para 41; ALINORM 97/24A, para 49).

The 1998 JMPR conducted a review of the toxicology of ethoxyquin. The present evaluation is within the CCPR Periodic Review Programme.

Information on residue chemistry and environmental fate was provided by the Northwest Horticultural Council (USA). The governments of Germany and The Netherlands submitted additional information.

IDENTITY

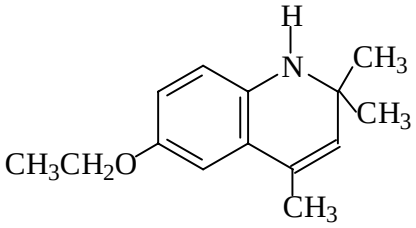
ISO Common name: ethoxyquin

Chemical name
- IUPAC: 1,2-dihydro-2,2,4-trimethylquinolin-6-yl ethyl ether
- CA: 6-ethoxy-1,2-dihydro-2,2,4-trimethylquinoline

CAS Registry No.: 91-53-2

Synonyms: ethoxyquine
ethoxychin (Czech)

Structural formula:



Molecular formula: $C_{14}H_{19}NO$

Molecular weight: 217.31

Physical and chemical properties

Pure active ingredient:

Appearance: brown slightly viscous liquid (Wojcieck, 1996)

Vapour pressure: $3.46x10^{-2}$ Pa ($2.60x10^{-4}$ mm Hg) at 25 C (Schetter and Kogovsek, 1996)
$1.18x10^{-1}$ Pa ($8.83x10^{-4}$ mm Hg) at 35 C
$3.32x10^{-1}$ Pa ($2.49x10^{-3}$ mm Hg) at 45 C

Boiling point: 150 C at 747 mm Hg (Wojcieck, 1996)

Octanol/water partition coefficient: 283 (log P_{ow} = 2.45) at 25 C (Lorence, 1996b)

Solubility at 25 C:

water	170 mg/l (Lorence, 1996c)
acetonitrile	462 g/l
n-octanol	452 g/l

Hydrolysis at 25 C:
pH 5 half-life = 3.7 days (Reynolds and Campbell, 1995)
pH 7 half-life = 6.7 days
pH 9 half-life = 9.3 days
Major degradation products (identified by LC-MS result from demethylation, desethylation at the ether linkage, and dimerization.

Technical material

Minimum purity: 97% (Schetter, 1996)

Stability: stable for 14 days at 55°C (Wojcieck, 1996) 15% loss under exposure to light for 14 days (Wojcieck, 1996)

Impurities: 6 impurities, each <0.5% w/w

Formulations

The commercially available formulation is an EC (emusifiable concentrate).

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

No studies were reported. None are required, as the only use of ethoxyquin is on pears post-harvest and neither pears nor pear by-products are significant animal feed items.

The 1998 JMPR reviewed the metabolism of ethoxyquin in rats. Parent ethoxyquin was not found in the urine, and only traces were found in faeces, liver, kidneys and adipose tissue, from rats given an intravenous dose. Some metabolites were identified in the urine and bile. The major metabolic pathway was O-de-ethylation at C-6 (yielding a phenol) and conjugation. The metabolic products in rats are different from those in plants (see below).

Plant metabolism

Anjou pears were washed with water and air-dried. A total of 144 pears, each 200 $\pm$ 30 g, were dipped for about 30 seconds in a solution prepared from an aqueous mixture of ring-labelled [^{14}C]ethoxyquin (unspecified amount, $\geq$93% purity by HPLC, radiochemical purity $\geq$99%, specific activity 98.6 mCi/mmol), Deccoquin 305 Concentrate (Elf Atochem, 52.3% ethoxyquin, 3,828 mg [^{12}C]ethoxyquin), and [2,4-^{13}C]ethoxyquin (1,277 mg, purity $\geq$98.5% by HPLC). The mixture was diluted to 257 ml with distilled water. The specific activity was 3659 dpm/μg or 1.65 μCi/mg. The [^{13}C]ethoxyquin served as a marker (+ 2 mass units) for GC-MS analyses. The pears were air-dried for 2 hours, and stored in an incubator at -2 $\pm$ 2.0°C and relative humidity >95% with constant air circulation. Incoming air was passed through a saturated sodium chloride solution and outgoing air was passed through a Tenax-TA trap.

The maximum label dosing concentration is 2.7 mg/ml. The test solution contained about 20 mg/ml, so its concentration was approximately 7.5 times the maximum label rate.

Eight pears were removed from storage at intervals of 0, 2, 7 and 14 days and 6, 8, 10, 12, 16, 20, 24, 28, and 33 weeks. Each of the pears was washed with methanol (70-100 ml) and the rinses analysed by LSC. Two whole pears were sliced, frozen with liquid nitrogen, and ground. The remaining six pears were peeled, and their combined peels and pulps were separately frozen with liquid nitrogen and ground. Triplicate aliquots of peel, whole pear, and pulp were combusted and the total radioactivity in each sample was measured.

Peel, pulp, and whole pear samples were extracted with methanol/water/chloroform (2.2:1:1) and the post-extraction solids (PES) were extracted with chloroform. All the extracts from each sample were combined, methanol/water and chloroform layers were separated and the ^{14}C in each fraction and the PES were determined. The nominal limit of detection was 0.01 mg/kg as ethoxyquin. The organic and aqueous extracts were then concentrated and analysed by HPLC and TLC.

The post-extraction solids from 33-week pulp, peel, and whole pear were each incubated in acetate buffer at 37°C with cellulase for a total of 26 hours. The hydrolysate was filtered, the aqueous fraction (Aq-1) was extracted with ethyl acetate to give EtOAc-1 and Aq-2, and the remaining solids (PES-2) were refluxed with 0.1 N NaOH for one hour to yield PES-3 and Aq-3. Aq-3 was extracted with ethyl acetate to yield Aq-4 and EtOAc-2.

Portions of the [^{14}C]ethoxyquin dosing solution were subjected to oxidation in air and by horseradish peroxidase. The products were extracted and analysed by TLC or HPLC.

HPLC was used both to analyse extracts and to isolate unknown degradation products. The instrumentation consisted of Nucleosil 5 C-18 100A, 4.6 x 250 mm column with a UV detector (254 nm) and a flow-through radioactivity detector in series and. Two mobile phase systems were used: (1) an isocratic mixture of acetonitrile and water (65:35) and (2) programmed elution from acidic water (0.25 ml H_3PO_4/l; A) to acetonitrile (B). The gradient was programmed from 100% A at 3 minutes to 100% B at 21 minutes. The flow rate for both systems was 1 ml/min. In some cases, the eluates were collected and analysed by LSC.

One-dimensional TLC was used to profile, quantify and purify extracts, with both normal-phase Si-60 F_{254} silica gel and reversed-phase Si-C-18F silica gel plates. Ethoxyquin and other reference standards were co-chromatographed as appropriate. The seven solvent systems used were detailed. The developed plates were examined with a radio-imaging system and non-radioactive spots were visualized with UV light.

Gas chromatography with a radioactivity monitor (RAM) and a flame ionization detector (FID) in parallel was used for the qualitative analysis of extracts and isolated unknowns. The column was a Restek Rt_x-1, 15 m x 0.25 mm i.d. Isolated unknowns were subsequently analysed by GC-MS on a similar column. Both quadrupole and magnetic sector instruments (EI mode) were used.

The total radioactive residues in the methanol rinses and extracts of peel, whole pear, and pulp at each sampling are shown in Table 1. The registrant provided adequate raw data to validate the findings.

The radioactivity in the rinses ranged from about 85% of the TRR in the whole pear on day 0 to about 10-20% after 12 weeks. The radioactivity in the rinsed peel reached about 35-50% of the TRR during weeks 10-33, and that in the pulp ranged from <2% on day 0 to 40-50% at weeks 12-24. The TRR in rinsed whole pears increased from 15% of that in unrinsed pears on day 0 to about 85-90% at weeks 12-33. This indicates translocation of the radioactive residue from the surface to the peel and pulp over a 12-week period.

The peel, pulp, and whole fruit extracts and post-extraction solids from each sampling were analysed for total radioactive residues. In the peel, 55-60% of the TRR was in the chloroform extract, about 20% in the methanolic aqueous extract, and about 25% in the PES. There was no pattern of changing distribution with time. Similar distributions with no consistent pattern of change with post-treatment interval were found in the pulp and whole pears.

The distribution of radioactive residues in the 33-week post-treatment samples of whole pear, pulp, and peel is shown in Table 2.

The methanol rinses at various intervals after treatment analysed by TLC and HPLC showed extensive degradation of ethoxyquin. Normal-phase TLC of 0-day, 2-day, and 6-week rinses revealed four distinct radioactive regions, including one attributable to the parent compound and one at the origin. Similar results were obtained when the TLC was conducted in an inert argon atmosphere. The HPLC radiochromatogram of the 0-day rinse showed ethoxyquin and an unknown eluting about 3.5 minutes earlier at a ratio of 1:4.2, unknown:ethoxyquin. HPLC radiochromatograms of the 28-day methanol rinse showed ethoxyquin, the early-eluting unknown, and at least 3 late eluters, including a major peak at approximately 34.5 minutes (1.4:1, unknown:parent). The 8-week radiochromatogram showed the 34.5 minute peak as the major component (2.2:1.0, unknown:parent). In a total of 6 discrete peaks two components were eluted before the parent and three components after it. The 33-week rinse showed only the 34.5 minute peak (62%) and a small amount of ethoxyquin (6%).

Table 1. Distribution of radioactivity in rinses and fractions of pears at intervals after treatment.

Post-treatment interval	Whole pear			Pulp			Peel (rinsed)	
	Rinse , % of TRR	Rinsed fruit, % of TRR	Total conc., mg/kg[1]	Rinse, % of TRR[2]	Rinsed pulp, % of TRR	Pulp, mg/kg	Peel , % of TRR	Peel, mg/kg
0 days	85.6	14.4	21.3	84.2	1.53	0.370	14.3	19.7
2 days	61.2	38.8	19.5	65.4	7.25	2.33	27.3	45.3

Post-treatment interval	Whole pear			Pulp			Peel (rinsed)	
	Rinse , % of TRR	Rinsed fruit, % of TRR	Total conc., mg/kg[1]	Rinse, % of TRR[2]	Rinsed pulp, % of TRR	Pulp, mg/kg	Peel , % of TRR	Peel, mg/kg
7 days	50.5	49.5	24.0	52.1	15.7	4.67	32.2	51.1
14 days	50.0	50.0	24.4	54.1	19.4	4.52	26.6	34.7
28 days	40.7	59.3	26.4	37.3	30.1	8.92	32.6	51.8
6 weeks	26.4	73.6	26.7	35.7	33.8	8.45	30.5	41.0
8 weeks	19.4	80.6	19.9	26.9	36.7	9.01	36.4	46.7
10 weeks	15.8	84.2	23.2	16.7	37.3	11.4	46.0	73.3
12 weeks	14.9	85.1	20.9	20.8	45.5	11.0	33.8	44.1
16 weeks	11.1	88.9	18.8	15.8	40.6	9.72	43.6	55.4
20 weeks	20.7	79.3	16.1	18.1	45.2	12.6	36.7	54.9
24 weeks	12.5	87.5	25.9	10.5	49.0	14.3	40.5	60.4
28 weeks	14.5	85.5	21.4	16.8	44.1	13.7	39.1	71.3
33 weeks	8.22	91.8	17.2	12.6	37.2	9.42	50.2	75.5

[1] As ethoxyquin. Average 21.8 $\pm$ 3.4 mg/kg, n = 14.
[2] Rinse of whole fruit, before peeling

The 32-minute unknown HPLC peak from the 8- and 33-week post-treatment rinses (the retention time had decreased with use of the column) was isolated by HPLC. Normal-phase TLC showed it to be the spot of highest R_f. The RAM gas chromatogram revealed a retention time of 22.7 minutes, compared to a 13.2-minute retention time for ethoxyquin. The GC-MS spectra of the isolated unknown in the 8- and 33-week rinses were identical. There was a molecular ion at m/z 432 and the ^{13}C compound at m/z 434. As the molecular weight of ethoxyquin is 217, the unknown mass spectrum is consistent with an ethoxyquin dimer (2 x 217-2). The relative abundances of ^{12}C and ^{13}C make it likely that the ^{13}C dimer would contain only one ^{13}C monomer. The fragment of greatest abundance was m/z 417, formed by loss of a CH_3 group. Other significant fragments were at m/z 173 and 201. No further isolations or identifications of the minor degradation products were attempted.

Table 2. Distribution of the radiolabel in the methanol rinse, extracts, and hydrolysates of pears 33 weeks after treatment.[1]

Fraction	Peel (TRR = 94.4 mg/kg as ethoxyquin)		Whole fruit (TRR = 17.2 mg/kg)		Pulp[3] (TRR = 9.42 mg/kg)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Methanol rinse	20.0	18.9	8.22	1.41	-	-
Chloroform extract	50.7	47.8	45.8	7.86	38.3	3.61
Water/methanol extract	11.8	11.1	27.0	4.63	23.0	2.17
PES-1[2]	22.6	21.3	35.7	6.12	34.2	3.22
Organic extract of cellulase hydrolysate	1.09	1.03	0.402	0.069	0.544	0.0513

Fraction	Peel (TRR = 94.4 mg/kg as ethoxyquin)		Whole fruit (TRR = 17.2 mg/kg)		Pulp[3] (TRR = 9.42 mg/kg)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Aqueous extract of cellulase hydrolysate	1.60	1.51	1.59	0.273	2.03	0.192
PES-2	22.3	21.0	35.89	6.16	31.0	2.92
Aqueous extract of base hydrolysate	13.3	12.5	22.2	3.81	23.8	2.24
PES-3	8.49	8.01	9.01	1.55	4.12	0.388
TOTAL (%)	107.8		115.4		93.4	

[1] Recalculated without normalization; registrant normalized each processing step to 100%
[2] PES-1 was sequentially hydrolysed with cellulase and 0.1 N NaOH (reflux, 1 h)
[3] Pulp constituted 80.7% (w/w) of the pear, peel 13.6%, 5.7% not identified

The methanol rinse of the 33-week post-treatment fruit (containing 1.4 mg/kg ethoxyquin equivalents) was reacted with methyl iodide (CH_3I) to methylate any amine groups. The product mixture was analysed by HPLC. The ethoxyquin dimer peak remained unchanged, but a new peak appeared at about 19 minutes. Both compounds were isolated and analysed by GC-MS. The 32-minute peak had the spectrum identified as ethoxyquin dimer. The 19-minute compound showed a base peak at m/z 446, 14 mass units higher than the base peak of the dimer. The registrant attributed the 19-minute peak to a C-N dimer and the 32-minute peak to an N-N dimer. A C-N dimer would have one secondary amino group available for methylation (+14); an N-N dimer could not be methylated; a C-C dimer would have two secondary amino groups available for methylation (+28, m/z 460).

The methanol rinses showed decreasing amounts of ethoxyquin with increasing storage periods as follows: day 0 58% of the TRR or 12.4 mg/kg, day 28 15% of the TRR or 3.87 mg/kg, week 8 3.9% or 0.77 mg/kg, and week 33 0.49% or 0.085 mg/kg.

The chloroform extracts of peel, pulp, and whole pear from various samples from day 0 to 6 weeks were analysed by normal-phase TLC. No ethoxyquin was detected at any post-treatment interval. The radiochromatograms showed polar material at the origin and an unknown with a lower R_f value than ethoxyquin. The pulp extracts also contained an unknown with a higher R_f than ethoxyquin. Extracts of a control pear fortified with the dosing solution and of a fortified solvent blank both showed substantial decomposition of ethoxyquin. The HPLC radiochromatograms of the chloroform extracts showed no parent compound and a complex product mixture, even from the 0-day sample. The 33-week peel extract showed 3 major late-eluting peaks (21% at 27.3 min, 28% at 30.6 min, and 11% at 31.8 min). The 33-week whole pear extract showed similar peaks representing 18%, 16%, and 11% of the TRR. The 32-min peak from the 33-week chloroform extracts of whole fruit, peel, and pulp was isolated by HPLC and analysed by GC-MS. The three spectra corresponded to that of the dimer isolated from the methanol rinse (molecular ion m/z 432 and base peak m/z 417). The GC-MS spectrum of the 30.6 min peak had a molecular ion m/z 416 and base peak m/z 401, suggesting a dimeric structure less one CH_4 unit. Attempts to purify the extracts by TLC resulted in decomposition.

The methanol/water extracts of 12-week pear and 33-week whole fruit, peel, and pulp samples were purified by SPE and analysed by TLC. Reverse-phase TLC showed only material at the origin. Normal-phase TLC revealed one smeared zone. No parent compound was evident. Extracts were also analysed by HPLC. The radiochromatograms showed a complex pattern of dispersed radioactivity, with no parent or other distinct major peaks. An extract of 10-week post-treatment pulp contained three late-eluting peaks that corresponded approximately in retention time to the 3 peaks from the chloroform

extracts of 33-week peel and whole pears. Attempts to isolate the components by TLC caused decomposition.

Cellulase digestion of the PES from the 33-week whole fruit, peel, and pulp released 2.6%, 2.7%, and 2.0% of the TRR respectively. An appropriate control (digestion of the sample without cellulase) was not run, and the activity of the cellulase was not demonstrated. Ethyl acetate extraction of the hydrolysis mixture recovered $\leq$1% of the TRR in all cases.

Subsequent base hydrolysis of the post-extraction solids released 14%, 25%, and 23% of the TRR from the peel, pulp, and whole fruit respectively. Very little of this radioactivity (<2%) was extracted from the aqueous phase by ethyl acetate. The aqueous extracts (Aq-4) were analysed by HPLC. All showed one major peak (>90% of the injected ^{14}C) in the 18-20-minute region. The registrant attributed this to a C-N or C-C dimer on the basis only of retention time. In the whole pear 100% of the radioactivity in the water fraction (22% of the TRR, or 3.8 mg/kg) was attributable to the dimer. The compound was not isolated.

About 40% of the TRR in whole pears after 33 weeks was identified as a mixture of C-N and N-N ethoxyquin dimers (62% x 8.22% in the methanol rinse + 28% x 45.8% in the chloroform extract + 100% x 22.2% in the base hydrolysate). About 0.5% of the TRR was identified as ethoxyquin, and an additional 2% was released by cellulase. About 27% of the TRR was characterized as a water-soluble complex mixture of polar compounds in the methanol/water extract, and about 7% of the TRR (from the chloroform extract) might be attributed to monomers such as dehydrodemethyl-ethoxyquin, methyl-ethoxyquin, and dihydro-ethoxyquin, but this identification was tentative and based solely on HPLC retention time patterns.

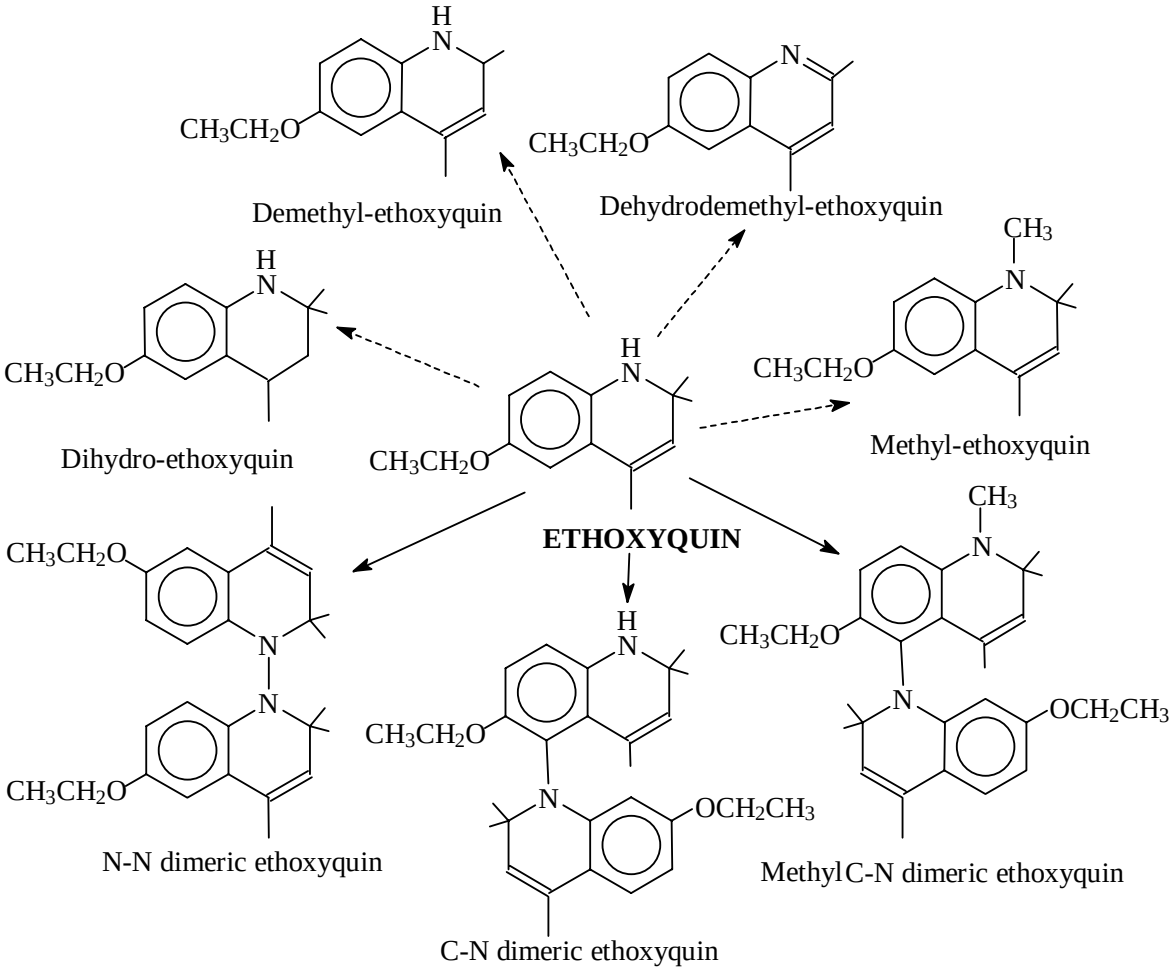
Various experiments were conducted on the dosing solution to identify possible degradation products. A methanol solution of [^{14}C]ethoxyquin was stirred in the air at room temperature for 2.5 days. The product mixture was analysed by TLC and HPLC. The latter showed peaks at 16.4, 17.8 and 35 min in addition to ethoxyquin at 20 min. The two early-eluting compounds were isolated and subjected to GC-MS. The 16 min compound showed four GC-MS peaks on the total ion chromatogram (spectrum nos. 665, 685, 699, and 723) at 11-12.5 min. Spectrum 665 showed a parent ion at m/z 219 and a base peak at m/z 204, consistent with dihydro-ethoxyquin. Spectrum 685, a major peak, had the same spectrum as ethoxyquin and may be from an ethoxyquin isomer. Spectrum 699 had a parent ion at m/z 201 and a base peak at m/z 173. This is consistent with 1-dehydro-2-demethylethoxyquin (Figure 1). Spectrum 723 had a parent ion at m/z 231 (ethoxyquin + 14), suggesting a methylated ethoxyquin (Figure 1).

The 17.8-minute HPLC peak from the oxidation of ethoxyquin was shown to be due to two compounds by GC-MS. Spectrum 686 was identical to that of ethoxyquin. Spectrum 699 had a parent ion at m/z 201, and was presumed to be the dehydrodemethyl-ethoxyquin found in the 16-minute HPLC peak. The compounds identified in the 16-18-minute retention time window may be among those found at similar retention times in the methanol rinses and chloroform extracts from the treated pears at the shorter storage periods, but this is speculative.

Treatment of [^{14}C]ethoxyquin with horseradish peroxidase (5 h, ambient temperature) transformed it to a more polar product whose HPLC retention time did not correspond to any of those in the pear extracts. No further work was conducted.

Figure 1. Proposed metabolic pathways of ethoxyquin in pears.

Dashed arrows indicate metabolism to products that have not been isolated or definitely identified.



Environmental fate

No studies were reported. As the only use of ethoxyquin is as a post-harvest dip treatment for pears exposure of the soil or ground water to ethoxyquin is unlikely. Rotational crops studies also have no practical benefit.

Analytical methods

In the US FDA Pesticide Analytical Method I (PAM Vol. II, Pesticide Reg. Sec. 180.178, 1975) peel or pulp (12 g) is extracted with iso-octane (200 ml) and 10% sodium carbonate (5 ml). The filtered iso-octane extract (50 ml) is partitioned with 0.5 N HCl (3 x 25 ml), the pH of the HCl extract is adjusted with 50% KOH, and the alkaline aqueous solution is extracted with iso-octane (3 x 25 ml). The combined iso-octane extracts are washed with water (25 ml), diluted to 100 ml and analysed in a photofluorimeter. The analysed solution (25 ml) is shaken with 0.04% potassium permanganate (15 ml) and the optical

density of the quenched iso-octane is measured. The second photofluorimeter reading is subtracted from the first. Calibration is with external standards containing known concentrations of ethoxyquin in iso-octane. The method was validated for pears at the limit of determination of 0.25 mg/kg.

The method was validated by dipping a Bosc pear in a solution of radiolabelled and natural-abundance ethoxyquin. The total ethoxyquin concentration was about 0.25%. The pear was dipped for 30 seconds, air-dried, ground with liquid nitrogen into a powder and stored on dry ice. Aliquots were radioassayed.

Three aliquots of the powder were analysed according to the PAM method. Aliquots of the extracts and washes were radioassayed and the final iso-octane extract was analysed with a luminescence/fluorescence detector. Excitation and emission maxima were 382 and 413 nm respectively.

The recovery of the radiolabel at each step of the procedure and a comparison of the results based on radioactivity with those based on fluorescence are shown in Table 3.

Table 3. Recovery of radiolabelled ethoxyquin by PAM Method 1 and comparison of results by measurement of radioactivity and by measurement of fluorescence.

Sample	% of total radiolabel				µg ethoxyquin in sample	
	Original iso-octane extract	Iso-octane after partition with HCl	Alkaline water after extraction with iso-octane	Final iso-octane extract	By radioactivity	By fluorescence
#1	72.4	1.1	2.0	69.8	565	976
#2	68.3	0.8	1.6	66.0	518	875
#3	85.0	1.1	1.4	82.2	677	1177
Mean	75.2	1.0	1.7	72.7	587	1009

The government of The Netherlands submitted two official methods for the determination of ethoxyquin in food commodities (Ministry of Health, Welfare and Sport, 1996). The first is a multi-residue GLC method. The sample is extracted with either ethyl acetate or acetone. Acetone extracts are partitioned with a second solvent, such as methylene chloride. There is no clean-up or derivatization. The gas chromatograph is equipped with a DB-1, DB-5, or DB-1701 capillary column.

The second method is specialized for ethoxyquin, and has been applied to apples and pears. A homogenized sample (25 g) is extracted with 100 ml hexane, 10 ml 10% sodium carbonate, and 10 ml 10% sodium ascorbate solution. The mixture is centrifuged and the hexane layer is retained. The hexane extract is analysed by HPLC on a 250 x 4.6 mm i.d. column packed with Polygosil 60-5, with a fluorescence detector (excitation 355 nm, emission 440 nm). The mobile phase is 1% 1-propanol in hexane at 1.0 ml/min. The recovery is reported to be 104 $\pm$ 3% for apples and 100 $\pm$ 0.8% for pears, at a fortification concentration of 2.1 mg/kg, n = 10. The limit of determination is stated to be 0.01 mg/kg.

A modified AOAC method (AOAC, 1987) has been used in residue trials by the Northwest Horticultural Council. Ten g of homogenized pear is mixed with 0.5 g ascorbic acid in a centrifuge tube and blended with acetonitrile (100 ml, 30 seconds). An aliquot of the extract is analysed by the standard AOAC HPLC procedure. The method was validated at 0.5 mg/kg.

Stability of pesticide residues in stored analytical samples

No data were presented. The pear results of the metabolism study indicate that ethoxyquin is not stable on frozen pears. The proportion of the total radioactive residue attributable to ethoxyquin decreased rapidly at 0°C, being 58% on the day of treatment, 15% after 28 days, 4% after 56 days, and 0.5% after 231 days.

Definition of the residue

The current definition is ethoxyquin. The pear metabolism study has shown that ethoxyquin is readily converted to dimers, polar water-soluble compounds, and the degradation products dehydrodemethyl-ethoxyquin, methyl-ethoxyquin and dihydro-ethoxquin. Even on the day of application, 42% of the ethoxyquin had been degraded.

The Meeting concluded that the residue for compliance with MRLs should be defined as ethoxyquin. The residue for the estimation of dietary exposure cannot be defined until the toxicities of the plant degradation products are known.

USE PATTERN

In the USA, a solution containing 2700 mg/kg ethoxyquin can be applied as a spray on a brush bed or conveyor rolls, or combined in a pack-out wax treatment. It is used post-harvest on pears to prevent scald.

Ethoxyquin has no uses on agricultural crops in Germany or The Netherlands.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Two post-harvest trials were conducted with Anjou pears in the state of Washington, USA, in 1996. The pears were in cold storage before the study. The pears were first soaked in a sodium phenyl orthophosphate bath and dried. The pears were passed through a commercial packing-line on a brush bed conveyor. In each trial ethoxyquin was applied as a wax spray at a concentration of 2700 mg/kg. An SC containing 52.2% ethoxyquin was diluted at 5 ml to 1000 ml water, to give about 0.26 kg ai/hl. The solution was discharged at a rate of 580 ml/min, which provided thorough coverage of the pears. A separate solution was prepared for each trial. The pears were passed through a drier, and duplicate samples of 16 treated and untreated pears were collected in each trial. The pears were halved, immediately frozen, and analysed within 18 days of collection.

The pears were analysed by the US FDA Pesticide Analytical Manual Vol. II method. A P&K Model 650-10S fluorimeter was used, with excitation and emission maxima of 359 nm and 430 nm respectively. Calibration was with external standards, 0.0075–0.18 µg/ml. Linear regression analysis with a forced zero gave typical r^2 values of 0.999. Two sets of validations were conducted before analysing the test samples, with control samples fortified with ethoxyquin at 0.25–5 mg/kg, and recoveries were also determined concurrently with the analysis of treated samples. The recoveries are shown in Table 4. The limit of determination is assumed to be 0.25 mg/kg.

Twelve additional trials in Washington State were conducted in 1999 by the Northwest Horticultural Council. A 51.3% SC was diluted with water to give a nominal 2700 mg ai/l. Organically grown pears stored at 0°C were warmed to room temperature and divided into groups of 20. The 20 pears used in each trial were placed in two plastic file boxes with large openings in the sides and bottom. The pears were sprayed with the 2700 mg/kg solution through four disc cone nozzles located 7.7 cm above the

fruits and spaced 2 cm apart. The spray was released at 1.3 bar. The pears were sprayed for 30 seconds, rotated 180°, and treated for a further 30 seconds. About 2.6 l was applied to each box of twenty.

Two groups of twenty pears were treated with a formulation blank as controls before running the ethoxyquin trials. Each trial was run with an independently prepared treatment solution. The application equipment was cleaned between treatments by rinsing the pressurized tank and nozzles with clean water.

Each group of twenty treated pears was allowed to drain dry and then divided into two sub-groups of 10 pears each. The stems were removed and the pears were individually wrapped in aluminum foil. Each group of ten was placed in a plastic bag, and the bags were vacuum packed and stored frozen pending analysis.

The pears were analysed by the AOAC method. Each group of ten was homogenized after freezing in liquid nitrogen and two 25 g sub-samples were taken from each trial for analysis. All samples were analysed within 14 days of collection. Both control samples contained <0.01 mg/kg. Validation and concurrent recoveries are shown in Table 4. The validated limit of determination was 0.5 mg/kg.

Table 4. Recovery of ethoxyquin from fortified pears.

Fortification, mg/kg	Recovery, %
Validation by PAM Method II	
0.25	107
0.5	104
1	81
3	90
5	98
0.25	107
0.5	86
1	97
3	75
5	94
Concurrent recoveries by PAM Method II	
0.5	69
3	76
5	86
0.25	99
0.5	92
3	89
0.25	129
0.5	91
3	98
0.25	99
0.5	92
3	89
Mean	92.4 $\pm$ 14.6%

Fortification, mg/kg	Recovery, %
Validation by AOAC method	
0.50	99
0.50	108
1.0	99
1.0	101
3.0	104
3.0	101
5.0	103
5.0	103
Concurrent recoveries by AOAC method	
0.566	104
5.44	95.8
1.07	95.3
3.11	84.2
1.03	106
2.96	97.6
0.949	92.3
1.00	92.5
Mean	96.0 $\pm$ 6.9 %

The results of the analyses of the treated pears are shown in Tables 5 and 6 .

Table 5. Residues of ethoxyquin on pears on the day of treatment with a wax containing 2700 mg/kg ethoxyquin applied with a brush bed conveyor.

Trial no.	Sample no.	Ethoxyquin, mg/kg
WA-48	1	0.37, 0.44 (0.40)
	2	0.25, 0.38 (0.32)
Average WA-48		0.36
WA-49	1	0.72, 0.61 (0.66)
	2	0.67, 0.66 (0.66)
Average WA-49		0.66

Table 6. Residues of ethoxyquin on pears on the day of treatment with an aqueous spray at a nominal concentration of 2700 mg/l.

Trial no.	Solution concentration, mg/l	Sample no.	Ethoxyquin, mg/kg
1	2400	1	1.39, 1.76 (1.58)
		2	1.69, 1.38 (1.54)
Average #1			1.56
2	2800	1	1.96, 1.61 (1.79)
		2	1.82, 1.51 (1.67)
Average #2			1.73
3	2800	1	2.22, 2.24 (2.23)

Trial no.	Solution concentration, mg/l	Sample no.	Ethoxyquin, mg/kg
		2	2.04, 2.40 (2.22)
Average #3			2.22
4	2900	1	1.81, 1.55 (1.68)
		2	2.12, 1.86 (1.99)
Average #4			1.84
5	2700	1	2.38, 2.19 (2.29)
		2	2.32, 1.89 (2.11)
Average #5			2.20
6	2900	1	1.73, 2.19 (1.96)
		2	2.35, 2.54 (2.45)
Average #6			2.20
7	2800	1	1.94, 1.86 (1.90)
		2	1.33, 1.78 (1.56)
Average #7			1.73
8	2900	1	1.74, 1.88 (1.81)
		2	1.84, 1.76 (1.80)
Average #8			1.80
9	2800	1	2.18, 2.33 (2.26)
		2	2.14, 2.14 (2.14)
Average #9			2.20
10	2800	1	1.54, 1.90 (1.72)
		2	1.45, 1.39 (1.42)
Average #10			1.57
11	2700	1	1.48, 1.55 (1.52)
		2	1.84, 1.60 (1.72)
Average #11			1.62
12	2800	1	2.00, 2.05 (2.03)
		2	1.32, 1.39 (1.36)
Average #12			1.70

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

There are no major processed commodities of pears in international trade.

Residues in the edible portion of food commodities

No information.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The government of The Netherlands reported that 500 apples in commerce were analysed in the period 1994–1996. None contained residues at or above the MRL, 3 mg/kg. Five had residues <0.05 mg/kg, the limit of determination.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed of the following national MRLs.

The Netherlands	
Apples	3 mg/kg
Pears	3 mg/kg
Other food Commodities	0.05 mg/kg (limit of determination)
USA	
Apples	3 mg/kg (pre-harvest and post-harvest use)
Pears	3 mg/kg (pre-harvest and post-harvest use)

APPRAISAL

Ethoxyquin, an antioxidant preservative, was first evaluated in 1969 and re-evaluated for toxicology in the CCPR Periodic Review Programme in 1998. It was scheduled by the 1995 CCPR for a periodic review of residue chemistry in 1999. The deletion of the CXL for pears treated post-harvest, the only use with a Codex MRL, was postponed pending the toxicological and residue chemistry reviews.

Data on residues and environmental fate were provided by the Northwest Horticultural Council (USA) and additional information was reported by the governments of Germany and The Netherlands.

Animal metabolism

No studies were reported. Since the only use is for the post-harvest treatment of pears and pears are not a ruminant or poultry feed item, studies of metabolism in ruminants and poultry are not needed.

At the 1998 Meeting, the WHO Core Assessment Group reviewed the metabolism of ethoxyquin in rats. Parent ethoxyquin was not found in the urine and only traces were found in the faeces, liver, kidneys and adipose tissue of rats given an intravenous administration. Some metabolites were identified in the urine and bile. The main metabolic pathway was *O*-de-ethylation, yielding a phenol, and conjugation .

The metabolic products in rats are different from those in plants.

Plant metabolism

Anjou pears were dipped in a solution containing unlabelled and [^{14}C]ethoxyquin (ring-labelled) at a concentration of 20 mg/ml, 7.5 times the maximum label rate. The pears were dipped in the solution for 30 seconds, air-dried for 2 hours and stored in an incubator at –2°C and relative humidity >95% with

constant air circulation. Eight pears were removed from storage at intervals of 0, 2, 7 and 14 days, and 6, 8, 10, 12, 16, 20, 24, 28 and 33 weeks.

The eight pears at each sampling were washed with methanol, two were sliced and ground at liquid nitrogen temperature, and the remaining six were peeled and the combined peels and pulps separately frozen and ground.

The whole pears, peel and pulp were each extracted with methanol/water/ chloroform (2.2:1:1). The post-extraction solids from the three 33-week samples were sequentially treated with cellulase and refluxing 0.1 N NaOH.

The samples were analysed by LSC, TLC, HPLC, GLC and GC-MS. The total radioactive residue (TRR) remained constant at 22 $\pm$ 3 mg/kg over the 14 sampling intervals, but the distribution among rinse, pulp and peel changed dramatically. The rinse contained 86% of the TRR on day 0 and this decreased to 50% on day 7 and 8.2% in week 33. The composition of the residue in the rinse changed from 58% ethoxyquin on day 0 to 0.49% in week 33. The residue in the peel increased from 14% on day 0 to 46% in week 10 and then fluctuated between 34 and 50% of the TRR. The residue in the pulp increased from 1.5% on day 0 to 16% on day 7 and to 49% in week 24. Thus, the radiolabelled residue was substantially translocated into both the peel and pulp.

The radiolabelled residue was readily isolated from the pear samples by a combination of solvent rinse, organic and aqueous solvent extractions, cellulase hydrolysis and base hydrolysis. In the pears stored for 33 weeks after treatment, 8% of the TRR was removed by a methanol rinse, 46% was extracted by chloroform, 27% was extracted by methanol/water,
2% was released by cellulase and 23% was released by mild base hydrolysis. The final post-extraction solid contained 9% of the TRR. Similar results were obtained at other storage intervals.

A significant proportion of the radiolabelled residue was identified by a combination of TLC, HPLC and GC-MS. In the pears stored for 33 weeks about 40% of the TRR (6.8 mg/kg as ethoxyquin) was identified as a mixture of C-N and N-N dimers. Only 0.5% (0.09 mg/kg) was identified as parent ethoxyquin. An additional 2% was characterized as released by cellulase and 27% of the TRR (4.6 mg/kg) was characterized by HPLC and TLC as a complex mixture of water-soluble polar compounds. Air oxidation of [^{14}C]ethoxyquin produced a residue that yielded TLC and HPLC chromatograms similar to those of rinses and extracts of [^{14}C]ethoxy- quin-treated pears. The residue is composed of degradation products (dehydrodemethyl-ethoxy- quin, *N*-methyl-ethoxyquin, dihydro-ethoxyquin) and this residue may constitute 7% of the TRR (1.2 mg/kg) in whole pears stored for 33 weeks.

The Meeting concluded that the metabolism and degradation of ethoxyquin on pears is adequately understood. Ethoxyquin is rapidly degraded or metabolized and the residue, but not ethoxyquin itself, is translocated into the pulp. Less than 0.5% of the total radioactive residue was ethoxyquin (in the methanol rinse) in treated pears stored frozen for 33 weeks.

No information was reported to the Core Assessment Group on the toxicology of the plant degradation products. They formed rapidly and were not observed in the rat metabolism study. The Meeting agreed not to recommend any MRLs, and recommended the withdrawal of the single existing CXL, until the toxicology of the degradation products in plants is known.

Environmental fate

No studies on environmental fate were reported, but none are required because ethoxyquin is used only in controlled indoor situations where entry into soil or water is very unlikely.

Analytical methods

The official US enforcement method consists in extraction of the whole fruit, peel, or pulp with iso-octane, clean-up by partition, and analysis with a photofluorimeter. The method was validated with labelled and unlabelled ethoxyquin, and used in pear trials at a limit of determination of 0.25 mg/kg.

The two official enforcement methods in The Netherlands are extraction and analysis by capillary column GLC (multi-residue method) and extraction with n-hexane and analysis by HPLC with a fluorescence detector. Acceptable recoveries were reported.

An AOAC HPLC method was validated at 0.5 mg/kg and used for data collection.

The Meeting concluded that adequate analytical methods exist for the determination of ethoxyquin in fruits for both enforcement and data collection.

Stability of residues in stored analytical samples

No studies were conducted, but the results of the metabolism study clearly indicate that ethoxyquin is unstable on pears stored frozen. Almost 50% of the ethoxyquin is lost on the day of application and 85% is lost by day 28 of frozen storage.

Definition of the residue

The current definition is ethoxyquin. The metabolism study has shown that ethoxyquin is readily degraded to dimers and probably to demethyl-ethoxyquin, methyl-ethoxyquin, dehydrodemethyl-ethoxyquin and dihydro-ethoxyquin.

The Meeting concluded that the residue for compliance with MRLs should be defined as ethoxyquin. The residue for the estimation of dietary exposure cannot be defined until the toxicities of the plant degradation products are known.

Residues resulting from supervised trials.

Fourteen trials on pears were conducted in the USA. GAP specifies post-harvest treatment with a 2700 mg/kg aqueous or wax spray on a brush bed or conveyor rolls. The trials were conducted at this rate, two with brush conveyor application of wax and twelve with an aqueous spray. Samples were frozen immediately and analysed within 14-18 days of treatment. The metabolism study indicates that a substantial loss of ethoxyquin (perhaps about 60%) may have occurred during storage.

The residues in rank order were 0.40, 0.66, 1.58, 1.72, 1.72, 1.79, 1.81, 1.90, 1.99, 2.03, 2.23, 2.26, 2.29 and 2.45 mg/kg. The Meeting estimated an STMR of 1.86 mg/kg and a maximum residue level of 3 mg/kg, but could not recommend the maximum residue level for use as an MRL.

Fate of residues in storage and processing

No storage or processing studies were reported, but ethoxyquin has been shown to be unstable on frozen pears and would be even more unstable on pears stored at temperatures above 0°C.

RECOMMENDATIONS

The Meeting concluded that an MRL could not be recommended. An STMR cannot be recommended in the absence of an MRL.

Definition of the residue for compliance with MRLs: ethoxyquin. The residue for the estimation of dietary intake cannot be defined until the toxicities of the degradation products in plants are known.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FP 0230	Pear	W	3 Po	-

FURTHER WORK OR INFORMATION

Desirable

1. Studies of ruminant or poultry metabolism.

2. A study of the stability of residues in stored analytical samples, with samples taken at intervals of hours up to 24 hours and then on alternate days.

DIETARY RISK ASSESSMENT

Chronic intake

No intake could be estimated because the Meeting recommended withdrawal of the single existing CXL.

Acute intake

The 1998 JMPR concluded that an acute RfD for ethoxyquin is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard, and residues are therefore unlikely to present an acute risk to consumers.

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FENAMIPHOS (85)

EXPLANATION

Fenamiphos was first reviewed by the JMPR in 1974, with subsequent residue evaluations published in 1977, 1978 and 1980. The compound was scheduled for periodic review at the 27th (1995) Session of the CCPR (ALINORM 95/24A Appendix IV). The 30th Session noted that the TMDI based on existing CXLs slightly exceeded the new ADI of 0.0008 mg/kg bw allocated by the 1997 JMPR.

The manufacturer submitted a comprehensive data package in support of the existing CXLs for banana, Brussels sprouts, cabbages, coffee beans, cotton seed, grapes, melons, oranges, peanut, pineapple and tomato. Additional data have been provided to support new residue limits for apple, cherries, lemons, limes, grapefruit, onions, peaches and peppers.

IDENTITY

ISO Common name: fenamiphos

Chemical name
IUPAC: ethyl 4-methylthio-*m*-tolyl isopropylphosphoramidate
CA: ethyl 3-methyl-4-(methylthio)phenyl (1-methylethyl)phosphoramidate

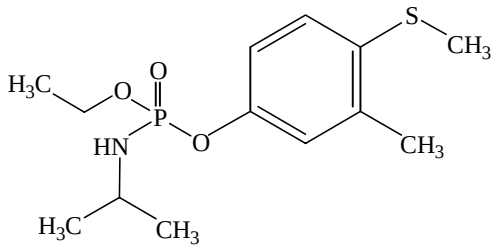
CAS No.: 22224-92-6

Synonyms: Nemacur, Bayer 68138

Molecular formula: $C_{13}H_{22}NO_3PS$

Molecular weight: 303.40 g/mole

Structural formula:



Physical and chemical properties

Pure active ingredient

Vapour pressure: 0.12 mPa (1.2×10^{-6} mbar) at 20°C; 0.23 mPa (2.3×10^{-6}mbar) at 25°C (Weber, 1984)

Melting point: 49°C (Klusacek *et al.*, 1986)

Purity:	99.6 molar percent (DTA); 99.5% elemental assay
Octanol/water partition coefficient:	2000 ± 370, log P_{ow} 3.30, at 20°C by HPLC (Krohn, 1984)
Solubility at 20°C:	water 0.4 g/l, 0.558 g/l (Battor *et al.*, 1984); hexane 10-20 g/l; dichloromethane, toluene and 2-propanol >200 g/l.
Specific gravity:	1.191 g cm^{-3} (Weber, 1987)
Hydrolysis at 25°C:	(sterile solution in dark), half-life 245 days at pH 5, 301 days at pH 7, 235 days at pH 9[1] (Mulford, 1987)
Photolysis:	half-life 3.6 hours at pH 7 (Dime *et al.*, 1983)
Dissociation constant:	does not show basic or acidic properties in water; not possible to specify pKa value in aqueous system (Stupp, 1992)
Thermal stability:	stable at room temperature (Klusacek *et al.*, 1986)
Henry's Law Constant:	1.2×10^{-4} $Pa.m^3.mole^{-1}$ at 20°C (Krohn, 1995)

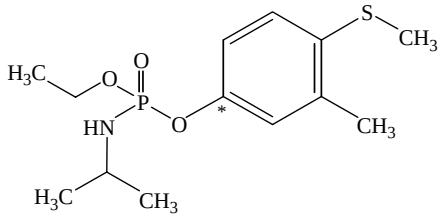
Technical material

Purity:	>92%; impurities total <10.5%

METABOLISM AND ENVIRONMENTAL FATE

Animal Metabolism

Rats. In a series of experiments by Ecker *et al.* (1989) male and female rats were dosed with [1-*phenyl*-^{13,14}C]fenamiphos either intravenously or orally. The position of the label is shown below.



The dose groups were as follows.

0.3 mg/kg bw, single intravenous low dose
0.3 mg/kg bw single oral low dose
One oral low dose of unlabelled compound/day for 14 days followed by a single oral low dose of the radiolabelled compound
3 mg/kg bw, single oral high dose

Urine from each animal was collected in the periods 0-4, 4-8, 8-24, 24-32 and 32-48 hours after administration. Faeces were collected in the periods 0-24 and 24-48 hours, and CO_2 was trapped

[1] K_d pH 5 = 2.81×10^{-3}; pH 7 2.3×10^{-3}; pH 9 2.95×10^{-3}.

in ethanolamine during 0-8, 8-24, 24-32 and 32-48 hours after administration. The following samples were taken *post mortem*: brain, heart, muscle, kidney, liver, skin, carcase, GI tract, lung, spleen, ovaries, uterus, testes and bone. Radioactivity was measured in all the samples by liquid scintillation counting and metabolites were quantified and identified by HPLC, GC-MS and/or NMR in all samples.

Urine was the major route of elimination in both male and female rats, with 93 to 100% of the administered radioactivity eliminated within 48 hours after dosing in all groups. The faeces contained 1.5 to 3.8% of the administered dose.

Low radioactive residues in the range 0.045 to 0.23% of the administered dose were found in the tissues and organs (excluding the GI tract). In all groups, the levels were below the limit of determination and the samples were not examined further.

The identified metabolites in the excreta accounted for more than 93% of the total recovered radioactivity, as shown in Table 1. The major metabolites were fenamiphos sulfoxide phenol (13-22% except in repeatedly dosed males where it accounted for only 4%) and its sulfate conjugate (40-54%), indicating that an important transformation pathway is oxidation of the methylthio group followed by cleavage of the isopropyl-nitrogen and aryl ester bonds.

Table 1. Metabolite distribution in the excreta of rats dosed with fenamiphos (Ecker *et al.*, 1989).

Compound	^{14}C, % of dose							
	0.3 mg/kg bw i.v.		0.3 mg/kg bw oral		14 × 0.3 mg/kg bw unlabelled + 1 x 0.3 mg/kg labelled		3 mg/kg bw oral	
	M	F	M	F	M	F	M	F
FSO	2.3	6.6		11.6	2.9		0.3	1.3
DIFSO			0.2	0.1		1.7	0.4	0.7
FP	8.4	3.5	9.6	0.8	5.3	9.8	4.6	4.0
FSOP	11.8	19.3	11.8	18.5	4.0	21.8	21.5	12.7
FSO_2P	4.5	2.6	3.8	3.0	1.9	4.9	10.8	6.5
FP-sulfate	19.3	15.8	6.9	8.2	5.3	4.9	6.1	5.7
FSOP-sulfate	40.2	44.0	53.7	42.5	48.4	45.3	43.4	40.3
FSO_2P-sulfate	7.8	4.2	7.9	7.9	15.1	7.5	10.0	11.5
OH-FSO_2P-sulfate	0.6	0.1		1.0	10.0			11.3
Identified	94.9	96.1	93.9	93.6	92.9	95.9	97.1	94.0
Unidentified	4.7	3.4	5.2	5.6	6.4	3.4	2.4	5.6
Solids	0.2	0.3	0.8	0.7	0.5	0.5	0.4	0.3
Body	0.2	0.2	0.1	0.2	0.2	0.2	0.1	0.1
Total	100	100	100	100	100	100	100	100

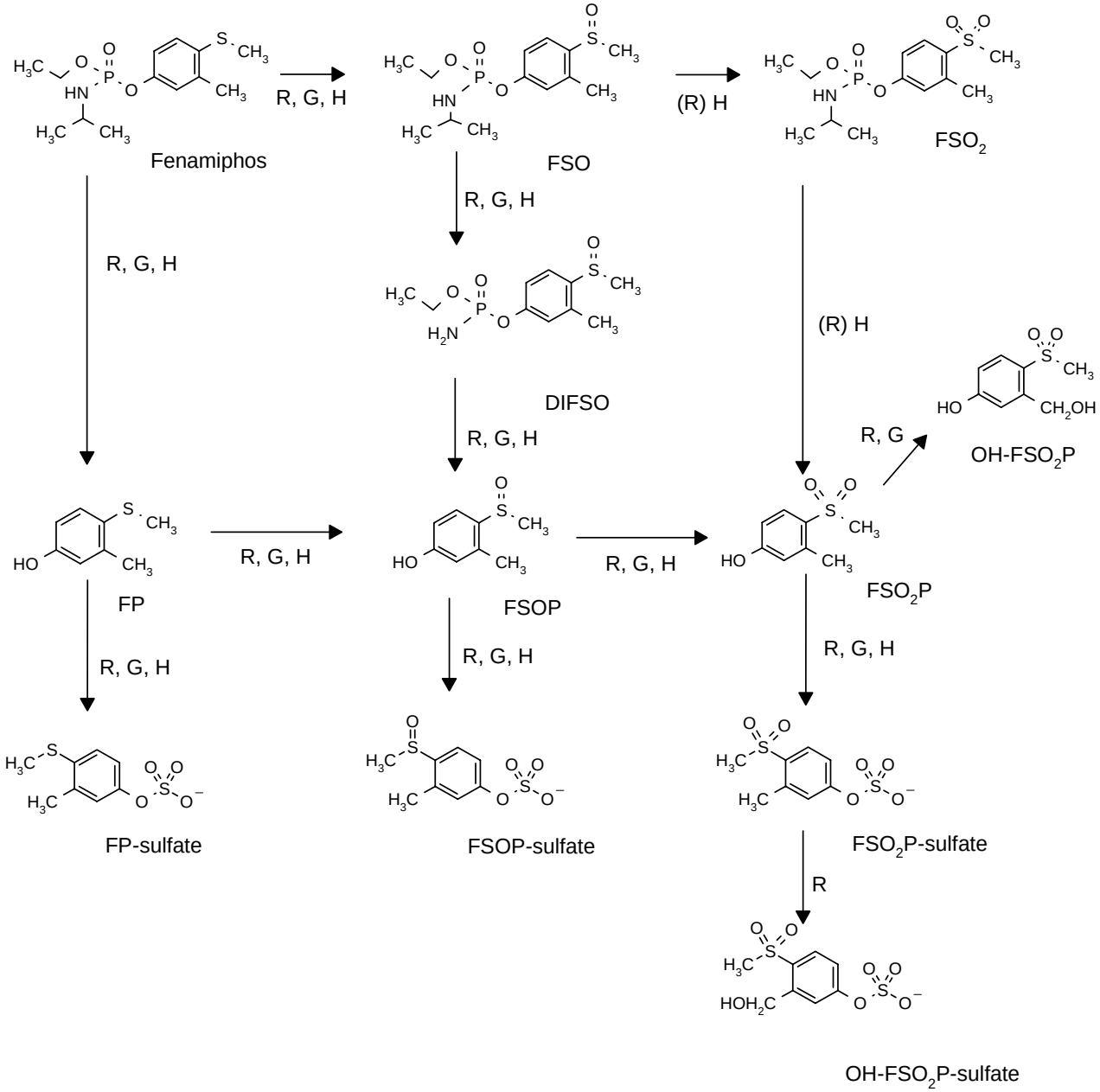
FP	fenamiphos phenol	FP-sulfate	fenamiphos phenol sulfate
FSO	fenamiphos sulfoxide	FSOP	fenamiphos sulfoxide phenol
FSOP-sulfate	fenamiphos sulfoxide phenol sulfate	FSO_2P	fenamiphos sulfone phenol
FSO_2P-sulfate	fenamiphos sulfone phenol sulfate	DIFSO	desisopropyl-fenamiphos sulfoxide
OH-FSO_2P	hydroxy-fenamiphos sulfone phenol sulfate		

The metabolite OH-FSO_2P-sulfate accounted for about 10% of the ^{14}C in the repeatedly dosed male and the high-dose female groups, but for $\leq$1% in the other groups. This metabolite is hydroxylated in either the phenyl ring or at the 3-methyl group. It is probably formed by direct hydroxylation of FSO_2P-sulfate. The proposed metabolic pathways of fenamiphos in animals are shown in Figure 1.

In an earlier series of experiments (Gronberg, 1969), groups of male and female rats received single oral doses of 2 or 2.8 mg/kg bw of labelled fenamiphos ([^{14}C]ethyl, [^{3}H]methylthio or [^{14}C]isopropyl) or 2 mg/kg bw [*ethyl*-^{14}C]fenamiphos sulfoxide or sulfone. The animals were monitored for 48 hours during which period urine, faeces, CO_2 and water vapour were collected and

Figure 1. Proposed metabolic pathway of fenamiphos in animals.

(R = rat, G = goat and cow, H = hen)



FP	fenamiphos phenol	FP-sulfate	fenamiphos phenol sulfate
FSO	fenamiphos sulfoxide	FSO_2	fenamiphos sulfone
FSOP	fenamiphos sulfoxide phenol	FSO_2P	fenamiphos sulfone phenol
FSOP-sulfate	fenamiphos sulfoxide phenol sulfate	FSO_2P-sulfate	fenamiphos sulfone phenol sulfate
DIFSO	desisopropyl fenamiphos sulfoxide		
OH-FSO_2P	fenamiphos sulfone phenol, hydroxylated in the 3-methyl group		
OH-FSO_2P-sulfate	fenamiphos sulfone phenol sulfate, hydroxylated in the 3-methyl group		

their ^{14}C content measured. Animals dosed at 2 mg/kg bw were killed 48 hours after dosing and those dosed at 2.8 mg/kg bw were killed after 0.5, 1, 2 or 4 hours, or 9 days.

As in the 1989 study, most of the dose was excreted within 12 to 15 hours, with no sex- or radiolabel-related effects being apparent. The main identified radioactive compounds were

fenamiphos sulfoxide phenol and fenamiphos sulfone phenol, accounting for 19-31% and 6-8.5% of the administered label respectively, but 6 to 44% remained uncharacterized. The total radioactivity in the liver, kidneys and fat varied with time (Table 2).

Table 2. Total radioactive residues in the tissues and organs of rats dosed with [*ethyl*-^{14}C]fenamiphos at 2.8 mg/kg bw.

Sample	^{14}C, mg/kg fenamiphos equivalents				
	0.5 hours	1 hour	2 hours	4 hours	9 days
Brain					0.3
Heart					0.3
Liver	4.1	17.7	6.7	11.1	1.4
Kidney	0.6	4.6	1.5	3.1	0.6
Fat	0.1	0.3	0.1	0.4	0.6
Muscle					0.2
GI tract					0.5

The distribution of radioactivity was also investigated by whole body autoradiography (Weber, 1988). Rats were dosed orally at 3 mg/kg bw and autoradiograms taken when they were killed after 0.5, 2, 8, 24 or 48 hours. After 0.5 hours radioactivity was detectable in almost all tissues and organs, with very high concentrations localised in the stomach and small intestine, bladder and kidneys. The distribution pattern was similar after 2 hours, but by 8 hours after administration the radioactive concentrations had decreased in all the tissues and organs.

The results support those of other studies, showing that fenamiphos is largely excreted from the body within a 12-hour period, with very low levels remaining in the tissues and organs after 9 days.

Dairy cow. Fenamiphos sulfoxide is a major plant metabolite and soil degradation product of fenamiphos. [U-*phenyl*-^{14}C]fenamiphos sulfoxide was orally administered to a dairy cow in a single dose of 0.8 mg/kg bw[1] (Gronberg *et al.*, 1974). Blood, urine and milk samples were taken at hourly intervals. Faeces were collected as eliminated. The cow was killed 4 hours after administration and samples of brain, heart, liver, kidney, muscle (round, loin, flank and shoulder), fat (omental, renal and subcutaneous) and gastrointestinal contents were taken for analysis. All samples were analysed for radioactivity by scintillation counting and chromatography (GPC, TLC and GLC) following appropriate work-up.

Approximately 88% of the administered dose was recovered from the urine, faeces, milk, tissues and rumen contents. Of the recovered dose, approximately 47% was in the rumen contents, 39% was eliminated in the urine and 1.4% found in the tissues. The distribution of the radioactivity in the tissues is shown in Table 3.

Metabolites were characterized in specific tissue samples. A large proportion of the radioactivity remained unidentified. Of the identified metabolites, unchanged fenamiphos sulfoxide and fenamiphos sulfoxide phenol were the major components of the radioactivity. Some fenamiphos was also detected in fat, liver, kidney and heart.

[1] Assuming daily feed consumption of 3% bodyweight, the equivalent dose is 26.7 ppm in the feed; animal weight 418 kg.

Table 3. Distribution of radioactivity in a dairy cow after a single oral dose of 0.8 mg fenamiphos sulfoxide/kg bw (Gronberg *et al.*, 1974). Percentages in italics were obtained by additional methanol extraction.

Sample (mg/kg as FSO)	^{14}C, % of total in sample						
	U	F	FSO	DIF/DIFSO	FP	FSOP	FSO_2P
Liver (0.099)	50	5.6	5.6		24.2 *29.2*	14.6 *21.2*	
Kidney (1.636)	47.2	0.9	3.7	5.4	20.8 *51.8*	18.5 *22.4*	3.5
Brain (0.013)							
Heart (0.037)	66	1.1		2.1	26.8	30.8 *34.1*	
Muscle					*13.0*	*31.7*	
Round (0.010)	62.9					31.6	5.5
Flank (0.011)							
Loin (0.010)							
Shoulder(0.010)							
Fat		25.3			*33.7*	*22.5*	
Renal (0.014)							
Subcutaneous (0.017)							
Omental (0.015)	65.2	18.1	4.3		5.9	6.5	

U	unknown	F	fenamiphos	FSO	fenamiphos sulfoxide
DIF	desisopropyl-fenamiphos	FP	fenamiphos phenol		
FSOP	fenamiphos sulfoxide phenol	FSO_2P	fenamiphos sulfone phenol		
DIFSO	desisopropyl-fenamiphos sulfoxide				

Radioactivity peaked at 0.061 mg/kg fenamiphos sulfoxide equivalents in the 4-hour milk samples. The identified components of the TRR were fenamiphos sulfoxide phenol (37 to 40%) and fenamiphos phenol (maximum 21%). The unidentified radioactivity amounted to 27 to 46%.

Peak radioactive levels in blood were 0.24 mg/kg fenamiphos sulfoxide equivalents at 1 hour after dosing and steadily decreased to 0.09 mg/kg at 4 hours. The major component of the radioactive residue was fenamiphos sulfoxide phenol at 55 to 74% of the recovered radioactvity.

In urine, fenamiphos sulfoxide phenol was the major identified residue at 60 to 70% of the recovered radioactivity during the 4 hours.

Lactating goat. A lactating goat was dosed orally with [*phenyl*-^{14}C]fenamiphos at 1 mg/kg bw (equivalent to 22.5 ppm in the diet assuming a total daily feed consumption of 4.4% bw) for three consecutive days (Abbink *et al.*, 1988a; Weber and Ecker, 1990). The goat was slaughtered at the peak plasma level (15 minutes) after the third dose and samples of liver, kidney, muscle (loin, round and flank) and fat (perirenal, omental and subcutaneous) were collected for analysis. Blood samples were taken 0.25, 0.5, 1, 2, 3, 4 and 6 hours after the first dose. Urine and faeces samples were collected 8 and 24 hours after each administration, *i.e.* immediately before the next dose. The animal was milked before each dose (am milking) and 8 hours later (pm milking).

Fractions of blood, milk and urine were analysed by liquid scintillation counting, and homogenized faeces and tissue samples by liquid scintillation counting after combustion[1]. HPLC was used in the identification of radioactive metabolites.

[1] Samples were combusted in a freeze-dried state (as in the rat metabolism study). It was shown that volatile radioactivity was 0.02% of the administered amount during 24 hours.

Peak plasma concentrations of ^{14}C were 0.60 μg/ml as fenamiphos 0.25 hours after the first dose and decreased to 0.12 μg/ml at 6 hours. A calculated half-life of 4.5 hours was reported for elimination from plasma over the 6-hour period that was monitored. A large proportion of the administered radioactivity was eliminated, as shown in Table 4.

Table 4. Elimination of radioactivity from a lactating goat (Abbink *et al.*, 1988a; Weber and Ecker, 1990).

Route of elimination	Dose no.	Time after first dose (h)	% of total administered dose	Total, %
Urine	1	0		
		8	23.83	
	2	24	8.94	
		32	19.16	
	3	48	9.54	**61.47**
Faeces	1	0		
		8	0.38	
	2	24	0.31	
		32	1.81	
	3	48	1.13	**3.63**
Milk	1	0		
		8	0.021	
	2	24	0.005	
		32	0.030	
	3	48	0.009	**0.065**
				65.17

Urine was the predominant route of elimination accounting for 61.5% of the total administered dose. Elimination via the faeces and milk accounted for 3.63% and 0.065% of the total dose respectively. The total radioactivity in the edible tissues and organs was reported as 0.3% of the administered dose; the total recovered radioactivity was 65.5%.

The distribution of the radioactivity in the tissues is shown in Table 5. The highest levels of radioactivity were found in the liver and kidneys, with very low levels in muscle and fat.

Table 5. Distribution of radioactivity in the tissues of a lactating goat.

Sample	μg/g ^{14}C as fenamiphos	% of TRR
Liver	0.129	0.0943
Kidney	0.041	0.044
Muscle		0.05 (total*)
Round	0.005	
Flank	0.004	
Loin	0.006	
Fat		0.16 (total*)
Perirenal	0.001	
Subcutaneous	<0.001	
Omental	<0.001	

*Calculated assuming 30% and 12% of bw for total body muscle and total body fat respectively.

The radioactive compounds were characterized further in milk, liver and kidney. Samples of milk taken 8 hours after the first and second doses were pooled, extracted and analysed. Samples of all three substrates were analysed 8 and 24 months after storage (2nd and 3rd analyses).

Milk was mixed with methanol, the sediment was filtered and washed again with methanol. The remaining extract was evaporated and the radioactive compounds separated from by preparative

HPLC. Separated radioactive fractions were compared with reference compounds by contaminants co-injection; purified extracts were identified by direct peak matching.

The radioactive compounds identified in milk, liver and kidney are shown in Table 6. Fenamiphos phenol derivatives and their sulfate conjugates, fenamiphos phenol sulphate, fenamiphos phenol sulfoxide sulphate and fenamiphos phenol sulfone sulphate, were the major metabolites found in milk; fenamiphos was not present. The analyses of milk and liver 8 and 24 months after the samples were initially analysed (Weber and Ecker, 1990) showed a different metabolic profile in the third analysis (24 months) from that in the first and second analyses, as shown in Table 6.

Table 6. Radioactive compounds in the milk, liver and kidneys of a lactating goat determined after 0, 8 and 24 months storage (2nd and 3rd analyses) (Weber and Ecker, 1990).

Compound	% of ^{14}C in sample, 3 determinations								
	Milk			Liver			Kidneys		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Fenamiphos (F)				6.42		38.79			
FSOP	5.52	4.17	52.75	13.23	15.58	14.42		5.76	11.34
FSOP-sulfate	36.42	39.94		5.79	14.08	6.60	21.96	30.97	34.66
FP			8.36			1.82			
FP-sulfate	18.48	18.27				16.20	14.12		
FSO_2P			30.36			1.49			
FSO_2P-sulfate	29.98	27.69					14.62		
FSO	2.84	3.09	2.14	31.58	51.14	16.36		16.05	15.11
DIFSO	2.00	2.08							
Total identified	95.24	95.24	93.61	51.02	80.80	95.68	50.70	52.78	61.11
Unidentified	1.53	1.13	3.61	2.07	7.78		4.61	8.26	9.23
Solids	1.66	1.32	0.77	9.61	3.05	3.25	2.11	2.51	3.82
Heptane phase			0.75		2.87	0.85	24.73	22.19	
Minor fraction	1.58	2.31	1.27	11.25	5.50	0.23		14.26	25.85
Losses				20.05			17.85		
Total	100.01	100	100.01	94	100	100.01	100	100	100.01

FP	fenamiphos phenol	FP-sulfate	fenamiphos phenol sulfate
FSOP	fenamiphos sulfoxide phenol	FSOP-sulfate	fenamiphos sulfoxide phenol sulfate
FSO_2P	fenamiphos sulfone phenol	FSO_2P-sulfate	fenamiphos sulfone phenol sulfate
DIFSO	desisopropyl-fenamiphos sulfoxide	FSO	fenamiphos sulfoxide

The major radioactive compounds in the liver were fenamiphos sulfoxide, fenamiphos sulfoxide phenol and its sulfate conjugate in the first and second analyses. In the third analysis, fenamiphos, fenamiphos sulfoxide phenol and fenamiphos phenol sulfate were the main compounds. In the first liver analysis, 20% of the radioactivity was lost and 11% was present in a minor fraction which was not further characterized.

In the kidneys fenamiphos sulfoxide phenol sulphate was the main residue in all three analyses, with fenamiphos sulfoxide and fenamiphos sulfoxide phenol also prominent in the second and third analyses and fenamiphos phenol sulfate and fenamiphos sulfone phenol sulfate prominent in the first. The third analysis did not differ significantly from the second, as it had in the liver. The total characterized radioactivity was low in kidney, as 22% and 25% of the ^{14}C was in the heptane phase from the 1st and 2nd analyses respectively and 26% was in the minor fraction in the 3rd analysis.

The radioactive compounds found in the muscle and urine are shown in Table 7. The metabolite composition in the flank muscle differed from that in loin and round muscle.

Table 7. Distribution of radioactive compounds in muscle and urine (Weber and Ecker, 1990).

Compound	% of total ^{14}C in			
	Muscle			Urine
	Round	Loin	Flank	
FSOP			33.7	0.3
FSOP-sulfate	25.0	25.7		27.7
FP-sulfate				13.8
$DIFSO_2$			28.2	
FSO_2P-sulfate	35.7	13.1	38.1	5.2
FSO	39.3	61.2		
Total identified	100	100	100	47

In urine, only 47% of the radioactivity was identified; 59% was characterized as an unidentified metabolite M1 and approximately 4% as unidentified metabolites M2 and M3.

Laying hens. Two groups of five hens were dosed orally with [1-*phenyl*-$^{13,14}C$]fenamiphos at a level of 1 mg/kg bw (equivalent to 10 ppm in the feed assuming a total feed intake of 10% bw/day as a maximum for hens) for three days (Abbink *et al.,* 1988b). Samples of blood were collected 0.25, 0.5, 1, 2, 4, 6 and 24 hours after the third dose. Excreta were collected at 24 hour intervals immediately before the next dose. Eggs were collected twice daily, in the morning before the dose and 8 hours after dosing. Eggs were also removed from the oviduct at slaughter.

The birds were killed 0.5 hours after the third dose and samples of kidney, liver, heart, gizzard (without lining and contents), skin (without subcutaneous fat), muscle (breast and thigh) and subcutaneous fat were taken for radioanalysis. All tissue samples were freeze-dried before combustion and liquid scintillation counting. HPLC was used for isolation and characterization of the radioactive compounds.

Radioactivity in the blood plasma reached a maximum of 0.44 μg/ml as fenamiphos (average 0.3 μg/ml) 0.5 hours after the third dose which decreased to 0.029 μg/ml (average 0.028 μg/ml) at 24 hours [1]. The dose was eliminated with a half-life of 4.3 hours over the 24 hour monitoring period.

The total recovered radioactivity in individual birds ranged from 64 to 73% of the dose with elimination in the excreta ranging from 60 to 70% of the administered radioactivity. Eggs contained a maximum of 0.03% of the radioactivity. The TRR in the tissues ranged from 1.74 to 4.85%. The distribution of radioactivity in the tissues and eggs is shown in Tables 8 and 9.

Table 8. Total radioactive residues in hen tissues and eggs.

Sample	^{14}C, μg/g as fenamiphos
Liver	0.613
Kidney	2.267
Heart	0.230
Muscle	
Thigh	0.104
Breast	0.062
Skin	0.138
Subcutaneous fat	0.092
Eggs	0.010, 0.012
Gizzard	0.251

[1] Reported in a subsequent study.

Table 9. Radioactive residues in eggs and tissues expressed as a percentage of total recovered radioactivity (Abbink *et al.*, 1988b).

Compound	% of total radioactivity in								
	Liver	Kidney	Heart	Skin	Fat	Thigh	Breast	Gizzard	Eggs*
Fenamiphos (F)	0.4	0.4	7.7	10.4	16.5	10.4	10.8	30.4	12; 14.1
FSOP	3.4	27.2	6.7	11.1	13.2	16.4	15.4	6.8	10.4; 3.4
FSO_2P	8.7	30.4	19.3	13.0	10.5	9.6	8.0	16.0	10.8; 8.7
FP	14.1	0.9			31.1	2.0	1.6	5.4	6.8; 14.1
DIFSO								23.0	
FSO						15.9	17.1	2.7	
FSO_2							10.7		
FP-sulfate	10.3	9.9	7.5	12.6	4.0	2.4	3.5	2.4	12.8; 10.3
FSOP-sulfate	3.8	9.6	8.5	16.7		4.7	4.0	3.0	10.6; 3.8
FSO_2P-sulfate	17.2	4.1	7.0	10.7		8.2	5.5	0.9	12.4; 17.2
Total identified	57.9	82.5	56.7	74.5	75.3	69.6	76.6	90.6	75.8; 71.6
Unidentified	14.6	4.2	11.2		8.7	7.2	1.9		12.5; 14.6
Total recovered	72.5	86.7	67.9	74.5	84.0	76.8	78.5	90.6	88.3; 86.2

FP fenamiphos phenol
FSO fenamiphos sulfoxide
FSOP fenamiphos sulfoxide phenol
FSO_2P fenamiphos sulfone phenol
DIFSO desisopropyl-fenamiphos sulfoxide
FP-sulfate fenamiphos phenol sulfate
FSO_2 fenamiphos sulfoxide sulfone
FSOP-sulfate fenamiphos sulfoxide phenol sulfate
FSO_2P-sulfate fenamiphos sulfone phenol sulfate
*First figures 24 hours and second figures 0.5 hours after third dose.

The main radioactive compounds in the tissues and eggs were generally fenamiphos sulfone phenol, fenamiphos sulfoxide phenol, fenamiphos phenol and their sulfate conjugates. Fenamiphos was also present in all the samples, and prominent except in liver and kidney.

In a subsequent study (Ecker and Weber, 1990) the radioactive residues in the eggs, liver and muscle were determined 8 and 24 months after the initial analyses. The results are shown in Table 10.

Table 10. Percentage distribution of radioactive compounds in the liver, muscle and eggs analysed initially and after 8 and 24 months storage (1st, 2nd and 3rd analyses; Ecker and Weber, 1990).

Compound	Liver			Muscle (breast)			Eggs		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Fenamiphos (F)	0.24	2.67	1.47	10.02	12.58	9.58	5.59; 9.67	5.63	13.35
FSOP	11.68	20.66	29.97	14.31	12.97	23.69	4.4; 2.05	16.26	23.14
FSOP-sulfate	9.34	3.43	6.23	3.70	9.14	5.61	4.74; 2.8	13.87	13.33
FP	2.98	1.68	1.47	1.42	2.44	2.59	3.25; 9.84		
FP-sulfate	6.24	4.66	3.98	3.3		3.73	5.95; 7.1	5.37	7.18
FSO_2P	22.22	25.20	25.34	7.42	8.13	18.88	5.64; 5.99	9.79	
FSO_2P-sulfate	3.93		1.73	5.12	7.29				
FSO		8.16	4.35	16.14	16.99	16.64	5.42 (0.5)	16.59	22.23
DIFSO	14.77								
$DIFSO_2$				9.98	10.23	0.86	4.23; 6.67	6.00	
Total identified	71.40	66.46	74.54	71.41	79.77	81.58	39.22; 44.62	73.51	79.23
Unidentified	8.33	12.37	8.97	16.80	6.36	2.76	18.23; 12.60	20.10	9.27
Solids	1.63	1.68	4.30	5.99	8.83	11.22	7.79; 6.56	4.93	8.10
Heptane phase	3.17	0.48	0.27	0.54	0.25	1.18	2.74; 4.91	6.58	3.49
Losses	18.63	19.44	12.19	5.79	5.04	4.43	35.39; 25.32	0.59	

Compound	Liver			Muscle (breast)			Eggs		
	1st	2nd	3rd	1st	2nd	3rd	1st	2nd	3rd
Total	103.16	100.43	100.27	100.53	100.25	101.17	103.37; 94.01	105.71	100.09

FP	fenamiphos phenol	FP-sulfate	fenamiphos phenol sulfate
FSO	fenamiphos sulfoxide	FSOP-sulfate	fenamiphos sulfoxide phenol sulfate
FSOP	fenamiphos sulfoxide phenol	FSO_2P-sulfate	fenamiphos sulfone phenol sulfate
FSO_2P	fenamiphos sulfone phenol	$DIFSO_2$	desisopropyl-fenamiphos sulfone
DIFSO	desisopropyl-fenamiphos sulfoxide		

Storage of liver and muscle for 8 and 24 months did not consistently affect the residue levels except those of fenamiphos sulfoxide phenol (FSOP) which increased. In muscle fenamiphos sulfone phenol increased also. In eggs, fenamiphos sulfoxide and its phenol increased.

The transformation pathways in rats, goats, dairy cows and hens show rapid oxidation of fenamiphos at the methylthio group to fenamiphos sulfoxide and fenamiphos sulfone. Both sulfoxide and sulfone are eventually eliminated after cleavage of the phosphate ester bond.

Plant metabolism

Beans. Mixtures of [*ethyl*-^{14}C]fenamiphos and [*methylthio*-^{3}H]fenamiphos were applied by stem injection or soil treatment to growing snap beans (Khasawinah, 1972a). For the stem injection 1 mg of the mixture in a ratio of $^{3}H:^{14}C = 9$ was applied to a site 5 cm above the ground on the main stem. The soil treatment was at a rate equivalent to 6.7 kg ai/ha with a ratio of $^{3}H:^{14}C = 9.6$. Each plant was placed in a glass growth chamber connected to acid and base traps and attached to an air pump. After 4 weeks the plants were extracted and the radioactivity in the extracts, the treated soil and the liquid in the traps was quantified by liquid scintillation spectrometry. TLC was used to separate the extracted mixtures, and was followed by enzymic and/or acid hydrolysis and gel permeation chromatography.

The distribution of the radioactivity from each treatment is shown in Table 11.

Table 11. Distribution of radioactivity in snap beans following stem injection or soil treatment.

Sample	% of applied ^{14}C	% of applied ^{3}H
Stem injection		
Extracted plant material	11	32
Solids	29.1	23.8
Water[1]	2.1	15.2
Acid trap		7.4
Base trap	38.2	
Total	80.4	78.6
Soil treatment		
Plant		
Extracted material	0.86	0.98
Solids	2.78	0.58
Water[1]	0.25	0.38
Traps		
Acid		1.26
Base	12.34	
Soil		
Extracted soil	66.22	68.13
Solids	24.06	24.06
Water		0.43
Drainage water	0.12	4.90
Total	107	101

[1] Aqueous phase remaining from the plant extraction

The results show that much of the radioactivity from the stem injection remained unextracted and was present in solids and volatiles caught in the base trap. About 90% of the radioactivity from the soil treatment remained in the soil and 24% was present in the solids after extraction; very little was present in the extracted plant material.

The distribution of the metabolites in the extracted plant material following the two treatments is compared in Table 12.

Table 12. Metabolites in snap bean extracts after treatment with ^{14}C- and ^{3}H-labelled fenamiphos (Khasawinah, 1972a).

Compound	% of total ^{14}C- or ^{3}H in sample			
	Stem injection		Soil treatment	
	^{14}C	^{3}H	^{14}C	^{3}H
FSO	30.8	10.8	39.5	34.5
FSO_2	23.7	9.7	24.8	29.6
FSOP		21.9		33.5
FSO_2P		40.8		
Non-polar	26.2	1.0	27.8	

The results show that the same metabolites were formed from both treatments apart from the high proportion of the sulfone phenol from the stem injection. Much of the radioactivity from the ^{14}C label remained in the non-polar fraction; further analysis indicated that it was probably incorporated into natural plant products.

In a subsequent study (Khasawinah, 1973a), 1 mg of ^{14}C-ring- and ^{3}H-methylthio-labelled fenamiphos in a ratio of ^{3}H:^{14}C of 4.1 was applied as a stem injection. The plant was placed in a glass chamber for 4 weeks. The experimental procedure was as before. The distribution of the radioactivity is shown in Table 13 and the identified metabolites in Table 14.

Table 13. Distribution of radioactivity in stem-injected snap beans (Khasawinah, 1973a).

Sample	% of applied ^{14}C	% of applied ^{3}H
Extracted plant material	35.4	35.4
Solids	24.8	24.8
Water	42.0	42.0
Acid trap		1.0
Base trap	1.0	
Total	103.2	103.2

The amount of radioactivity in the extracted fraction and the aqueous phase was higher than in the previous study, and less volatile material was produced. Enzymic hydrolysis of the aqueous phase revealed that the activity was predominantly due to glucose conjugates of fenamiphos sulfoxide and fenamiphos sulfone phenols.

Table 14. Metabolites in beans after stem injection with ^{14}C- or ^{3}H-labelled fenamiphos.

Compound	% of applied ^{14}C or ^{3}H
FSO	41.9
FSO_2	23.6
FSOP	15.7
FSO_2P	11.9
TLC origin	6.9

The ^{14}C:^{3}H ratio remained identical to that in the administered mixture. Overall, the metabolite composition has not changed much from that found in the previous study, although 100% of the applied radioactivity was recovered.

Bean plants were treated by stem injection or uptake from solution with 1 mg/plant of labelled fenamiphos (Pither and Gronberg, 1977). The following label combinations were used.

[^{3}H]ethyl[^{14}C]phenyl; ratio ^{3}H:^{14}C = 10
[^{3}H]isopropyl[^{14}C]phenyl; ratio 3H:^{14}C = 10
[^{3}H]methylthio[^{14}C]isopropyl; ratio ^{3}H:^{14}C = 10
[^{3}H]methylthio[^{14}C]isopropyl; ratio ^{3}H:^{14}C = 5

The plants were harvested at intervals after treatment, extracted with methanol, and the extract partitioned with water into methyl chloride. The organic and aqueous fractions were radioassayed and the remaining solids were combusted. The extracted radioactive compounds were characterized by GLC, HPLC and/or GC-MS. The distribution of the radioactivity in various fractions is shown in Table 15.

Table 15. Distribution of radioactivity in extracts of treated bean plants (Pither and Gronberg, 1977).

Label	Treatment	DAT[1]	% of radioactivity in sample		
			Aqueous	Organic	Insoluble
[^{3}H]ethyl + [^{14}C]phenyl	Stem injection (ethanol)	4	10	80.1	9.9
		7	20	56.6	22.8
[^{3}H]isopropyl + [^{14}C]phenyl	Stem injection (ethanol)	4	7.2	76.8	16.0
		7	28.8	48.6	22.6
[^{3}H]ethyl + [^{14}C]phenyl	Stem injection (glycerol)	7	41.7	49.5	8.8
		14	54.3	35.9	9.8
[^{3}H]isopropyl + [^{14}C]phenyl	Stem injection (glycerol)	7	33.5	45.1	21.4
		14	63.0	25.7	11.3
[^{3}H]methylthio + [^{14}C]isopropyl	Stem injection (glycerol)	7	24.0	68.7	7.3
		7	21.0	71.0	8.0
[^{3}H]ethyl + [^{14}C]phenyl	Solution uptake	7	9.8	81.9	8.3
		14	5.2	72.3	22.6
		21	25.9	56.9	17.3
[^{3}H]isopropyl + [^{14}C]phenyl	Solution uptake	7	16.6	76.2	7.2
		14	7.3	80.9	11.8
		21	15.9	70.1	14.0

[1]Days after treatment

Most of the radioactivity was generally in the organic extracts regardless of the treatment and the identity of the radiolabel. Stem injection with glycerol[1] transferred more radioactivity into the aqueous phase than the corresponding treatment with ethanol. The distribution of the metabolites in the organosoluble fraction is shown in Table 16.

Table 16. Percentage distribution of radioactivity in organosoluble residues of fenamiphos in treated bean plants.

Treatment and label	DAT	% of radioactivity in sample					
		F	FSO	FSOP	FSO_2	FSO_2P	DIFSO
Stem injection							
[^{3}H]ethyl + [^{14}C]phenyl	4	17.4	31.4	4.9	13.3	6.4	3.6
[^{3}H]isopropyl + [^{14}C]phenyl	4	10.9	30.8	6.8	12.5	11.1	3.6
[^{3}H]ethyl + [^{14}C]phenyl	7	14.2	19.8		8.6		3.8
	14	9.1	13.4		4.3	1.5	2.7
[^{3}H]isopropyl + [^{14}C]phenyl	7	6.6	17.5	4.3	7.7		3.0

[1] Glycerol stem injection 9:1 glycerol/H_2O; ethanol stem injection 1:1 ethanol/H_2O.

	14	2.3	11.1	1.8	4.5		2.5
[^{3}H]methylthio + [^{14}C]isopropyl	7	12.3	41.6		13.5		0.4
Solution uptake							
[^{3}H]ethyl + [^{14}C]phenyl	7	62.6	15.4				1.7
	14	31.8	22.8	10.9	5.2		0.9
	21	15.7	21.5	6.5	5.2	3.2	1.3
[^{3}H]isopropyl + [^{14}C]phenyl	7	46.5	18.8		7.6		
	14	51.5	18.0	5.6	4.5		0.6
	21	26.0	26.9	7.5	5.5		0.6

The results are in broad agreement with those from the previous study, with fenamiphos sulfoxide and fenamiphos sulfone generally the main metabolites after both injection and solution uptake. Fenamiphos was the predominant compound from solution uptake after 7 to 14 days.

Tomatoes. In two experiments, labelled fenamiphos was applied to the soil round tomato plants at a rate equivalent to 6.72 kg ai/ha 20 to 30 days before ripening of the fruit (Khasawinah, 1973b). In one experiment [^{14}C]ethyl- and [^{3}H]methylthio-labelled fenamiphos (ratio ^{3}H:^{14}C = 9.6) was applied to plants growing outdoors, and in the other the labels were [U-^{14}C]phenyl and [^{3}H]methylthio (^{3}H:^{14}C ratio = 4.1) and the fenamiphos was applied to glasshouse plants. Tomatoes were harvested for analysis as they ripened and foliage samples were also taken. Two varieties were used in the outdoor experiment. The results are shown in Tables 17 and 18.

Table 17. Distribution of radioactivity in extracts of treated tomatoes (Khasawinah, 1973b).

Treatment	Variety	DAT	% of radioactivity in sample		
			Aqueous	Organic	Insoluble
[^{14}C]ethyl + [^{3}H]methylthio (Outdoors)	Roma	22	32.5	46.5	20.9
		30	31.1	42.0	26.9
		37	27.5	38.5	33.9
		42	31.8	33.6	34.5
	Valiant	23	27.9	51.4	20.8
		37	30.9	40.8	28.3
		44	34.5	29.5	36.0
		50	41.9	24.5	33.6
		50*	17.1	50.4	32.5
[U-^{14}C]phenyl + [^{3}H]methylthio (Glasshouse)		10	16.5	82.4	1.1
		34	50.5	42.4	1.3
		46	52.7	45.6	1.7
		66	64.4	33.6	2.0
		74	64.8	32.4	2.8

* foliage

The distribution of the radioactivity from ethyl- and ring-labelled fenamiphos differed, particularly in the percentage of radioactivity found in the insoluble fractions and in the increase of the ring label in the aqueous fractions with time.

Table 18. Distribution of radioactivity in organic extracts of tomato fruit and foliage

Treatment	DAT	% of radioactivity in sample				
		F	FSO	FSOP	FSO_2	FSO_2P
[^{14}C]ethyl + [^{3}H]methylthio	22	8.33	76.7		13.3	
(Outdoors)	30		90		5.4	
Roma variety	37	7.5	69		8	
	42	6.3	56.7		11.7	
Valiant variety	23		69.2		19.2	
	37	6.9	65.9		11.1	
	44		54.9		19.5	

	50		50		22.6	
	50*		50		9.1	
					40.0	
[U-^{14}C]phenyl+ [^{3}H]methylthio	10	5.3	81.3		10.0	
(Glasshouse)	34	8.9	57.8	5.2	15.9	7.0
	46	7.9	58.9	3.2	12.1	5.8
	66		66.7	3.3	18.3	5.0
	74		75	3.7	10.0	6.2

* foliage

Fenamiphos sulfoxide and fenamiphos sulfone were the main compounds found in the organic extracts. The percentages found do not differ greatly between the ethyl- and ring-labelled compounds or between the two varieties. The phenol derivatives were identified in the glasshouse crops at levels below 10% of the extracted ^{3}H. The glasshouse and outdoor experiments were monitored for 74 and 50 days respectively. The data confirm that oxidation at the methylthio group followed by cleavage of the phosphate bond is the primary metabolic pathway in tomatoes.

Carrots. Carrots were transplanted into soil treated with a mixture of [^{14}C]ethyl- and [^{3}H]methylthio-labelled fenamiphos at a rate equivalent to 10.08 kg ai/ha (Khasawinah, 1973c). The plants were grown under field conditions and harvested 53, 67 and 86 days after treatment. The carrots were separated from the foliage before extraction and analysis. The radioactivity was distributed among the aqueous and organic phases and remaining solids as shown in Table 19.

Table 19. Distribution of radioactivity in extracts of carrots and foliage (Khasawinah, 1973c).

Sample	DAT	% of radioactivity in sample		
		Aqueous	Organic	Insoluble
Carrots	53	25	40.1	34.1
	67	18.5	26.2	55.4
	86	22.4	29.8	47.8
Foliage	53	25.2	38.6	36.2
	67	19.6	22.2	58.2
	86	19.2	15.2	65.7

Much of the radioactive residue was insoluble. Hydrolysis of the aqueous fraction with β-glucosidase showed that 49-69% and 44-76% of the water-soluble residue in carrots and foliage respectively was mainly composed of phenol sulfoxide and sulfone phenol conjugates. No unchanged fenamiphos was found.

Cabbage. In two experiments (Khasawinah, 1973d) cabbage seedlings were transplanted into soil treated either with fenamiphos labelled with 1-ethyl-^{14}C and methylthio-^{3}H at a rate equivalent to 13.44 kg ai/ha (I) or [U-*phenyl*-^{14}C] and [*methylthio*-^{3}H]fenamiphos at a rate equivalent to 33.59 kg ai/ha (II). The C:H ratios were 9.6 and 4.4 respectively. Cabbage heads were harvested at intervals for analysis. The distribution of radioactivity among the extract fractions is shown in Table 20, and among the metabolites in Table 21.

Table 20. Distribution of radioactivity in treated cabbage (Khasawinah, 1973).

Label and sample	DAT	% of radioactivity in sample		
		Aqueous	Organic	Insoluble
[^{14}C]ethyl + [^{3}H]methylthio (I)				
Outer leaves	36	2.4	67.9	29.8
	71	26.1	27.5	46.3
Inner leaves	36	3.1	66.3	30.5
	71	35.3	17.6	47.1
Whole head	61	29.5	34.6	35.9

[^{14}C]phenyl + [^{3}H]methylthio (II)				
Whole head	50	47.0	51.5	1.8
Inner leaves	90	48.1	45.7	6.2

The results of experiment I clearly show that as the cabbage matures the percentages of water-soluble and insoluble radioactivity increase while the proportion of organosoluble activity decreases. In experiment II, as a result of the higher rate of application the pattern of distribution is similar after 50 and 90 days.

Table 21. Radioactive metabolites in the organic phase from extracted cabbage.

Label and sample	DAT	Radioactivity, mg/kg as fenamiphos					
		FSO	FSOP	FSO_2	FSO_2P	Origin	Rf >0.6
[^{14}C]ethyl + [^{3}H]methylthio (I)							
Outer leaves	36	1.35		0.23		1.05	0.23
	71	0.19	0.62	0.25	0.78	0.11	0.23
Inner leaves	36	0.28		0.09		0.42	0.08
	71	0.02		0.01		0.01	0.03
Whole head	61	0.09	0.09	0.04	0.09	0.06	0.08
[U-^{14}C]phenyl+ [^{3}H]methylthio (II)							
Whole head	50	6.08	0.44	1.10	0.39	3.17	ND
Inner leaves	90	0.32	0.01	0.03	0.01	0.04	ND

The main identified components of the residue were fenamiphos sulfoxide and fenamiphos sulfone or the corresponding phenols, but comparable levels of radioactivity were found at the TLC origin.

Enzymatic hydrolysis of the aqueous fraction indicated that the water-soluble metabolites were predominantly glucoside conjugates of the phenol derivatives. Radioactivity in the insoluble fraction was released by acid digestion and found to be associated with the metabolites found in the organic fraction.

The transformation pathways in cabbages are similar to those found in tomatoes, beans and carrots, namely oxidation at the methylthio group and cleavage of the phosphate bond to give phenol derivatives of the sulfoxide and the sulfone and their water-soluble conjugates.

Pineapples. Pineapple plants were treated with labelled fenamiphos by stem injection, soil drench or spray according to the regimes shown in Table 22 (Flint, 1973).

Table 22. Treatment regimes in pineapple metabolism experiments (Flint, 1973).

Experiment/Label	Treatment	Rate	Sampling (DAT)
I [^{14}C]ethyl + [^{3}H]methylthio-	Stem injection	10.02 mg/plant	1, 5, 10 and 18
II U-phenyl-^{14}C + [^{3}H]methylthio-	Stem injection	10.02 mg/plant	1, 5, 10 and 16
III U-phenyl-^{14}C-	Soil application	22.4 kg ai/ha	15, 30, 60 and 90
IV U-phenyl-^{14}C-	Spray	0.89-1.1 kg ai/ha	1, 5, 10 and 30
V [^{14}C]ethyl + [^{3}H]methylthio-	Spray	0.89-1.1 kg ai/ha	15 and 30

The stem injection was applied to the centre of the fruit stalk and the soil application was poured around the base of each plant. Whole pineapple plants were collected at sampling and stalk, fruit and foliage were extracted for analysis. Soil samples from experiment III were also analysed. The results are shown in Tables 23-25.

Table 23. Distribution of radioactivity in soil and foliage after treatment of pineapples.

Treatment	Rate	DAT	Radioactivity, mg/kg as fenamiphos	
			Soil	Foliage
Soil application III	22.4 kg ai/ha	15	24.10	0.11
		30	2.10	0.27
		60	5.20	0.12
		90	4.90	0.32
Spray IV	≈1.1 kg ai/ha	1	0.09	14.46
		5	0.05	3.68
		10	0.82	7.26
		30	0.48	3.53
Spray V	0.89 kg ai/ha	15	0.09	4.82
		30	1.77	1.57
Stem injection I	10.02 mg/plant	18	0	1.14
Stem injection II	10.02 mg/plant	16	0.005	0.23

Table 24. Distribution of radioactivity in extracts of pineapple fruit.

Treatment	DAT	% of radioactivity in sample		
		Aqueous	Organic	Insoluble
Stem Injection I	1	7.7	76.9	15.38
	5	20.0	76.0	4.0
	10	14.8	62.9	22.2
	18	57.5	31.2	11.2
Stem Injection II	1	12.5	83.3	4.2
	5	2.8	11.3	1.4
	10	46.1	46.1	7.7
	16	35.0	50.0	15.0
Soil Application III	15	15.0	47.5	37.5
	30	25.6	60.0	14.4
	60	55.3	10.9	34.0
	90	58.6	8.1	33.3
Spray IV	1	3.5	92.9	3.5
	5	9.8	89.1	1.0
	10	15.1	73.6	11.3
	30	29.2	62.5	8.3
Spray V	15	14.8	78.8	6.3
	30	17.5	76.3	11.4

For all treatments the results show a general increase in water-soluble radioactivity with an associated decrease in organosoluble radioactivity with time. A high proportion of the radioactive material in the fruit was organosoluble. Its constituents in experiments III and IV are shown in Table 25.

Table 25. Organosoluble radioactive residues in treated pineapple plants.

Treatment and sample	DAT	^{14}C, µg/kg (ppb) as fenamiphos for F, FSO and FSO_2; as fenamiphos phenol for FSOP and FSO_2P					
		F	FSO	FSOP	FSO_2	FSO_2P	Unknown
Soil application III	15		0.0017	0	0.1	0	0.0001
	30		0.009	0.0001	0.0002	0.0001	0
	60		0.0035	0.0002	0.0004	0.0002	0.0001
	90		0.0044	0.0001	0.0006	0.0004	0
Spray IV							
surface	1	0.94	1.32	0.01	0.02	0.01	
pulp	1	0.05	0.05	0.001	0.001	0.001	
surface	5	0.85	2.41	0.04	0.11	0.02	
pulp	5	0.05	0.28	0.002	0.02		
surface	10	0.15	1.27	0.03	0.12	0.02	
pulp	10	0.02	0.25	0.01	0.03	0.002	
surface	30	0.05	1.16	0.05	0.17	0.03	
pulp	30	0.001	0.02	0.001	0.003	0.001	

The metabolites identified in fruit from the stem injection treatments were predominantly fenamiphos sulfoxide and sulfone and their phenols. In experiment II fenamiphos sulfoxide, fenamiphos sulfone and their phenol derivatives accounted for 48.5, 1.8, 18 and 4% of the radioactivity in the fruit respectively.

In enzymatic hydrolysates of the aqueous fractions from extracts of fruit treated by stem injection and spraying, 14 to 34% and 6 to 14% of the TRR was identified as fenamiphos sulfoxide phenol and fenamiphos sulfone phenol respectively.

In summary the data show that the metabolites in pineapple fruit are similar to those found in other plants, namely fenamiphos sulfoxide and sulfone and their phenol derivatives, irrespective of the application method. The main transformation pathway is stepwise oxidation at the methylthio group followed at each stage by cleavage of the phosphate group to leave the corresponding phenolic compounds.

Waggoner (1972) treated tomatoes, potatoes, beans and peanuts with labelled fenamiphos and identified the metabolites fenamiphos sulfoxide and fenamiphos sulfone by IR and mass spectrometry.

Tobacco seedlings were treated with [*ethyl*-^{14}C]- and [*methylthio*-^{3}H]fenamiphos at a rate equivalent to 11.2 kg ai/ha either a week before or a week after transplanting and grown indoors or outdoors (Khasawinah, 1971). Leaves collected 7 to 70 days after treatment were analysed. Radioactivity was also determined in cured leaves.

The radioactive residue was mainly composed of fenamiphos sulfoxide and fenamiphos sulfone, at levels ranging from 60 to 92% and 8 to 40% of the applied radioactivity respectively in plants after transplanting, and from 55 to 95% and 5 to 45% when treament was before transplating. Curing the leaves for 50 to 100 days resulted in some loss of radioactivity.

Rotational crops

Soil was treated with [^{14}C]ethyl- and [^{3}H]methylthio-labelled fenamiphos at a rate equivalent to 11.2 kg ai/ha and tobacco plants were grown in the soil for 70 days (Khasawinah, 1972b). The soil was maintained in the laboratory for 3 months, then stored in a freezer for 10 months. The TRR in the soil was then 1.7 mg/kg fenamiphos equivalents. Dilution with untreated soil resulted in residues as fenamiphos of 0.65 mg/kg fenamiphos sulfoxide, 0.07 mg/kg fenamiphos sulfone and 0.18 mg/kg unextractable. Soya bean plants were grown in the treated soil for 150 days and seedlings were removed 19 days after planting. Seedlings and samples of leaves, stems, shells and seeds from mature plants were extracted (Table 26).

Table 26. Distribution of radioactivity in extracts of soya bean plants grown as a rotational crop.

Sample	Radioactivity as mg/kg		
	Aqueous (as FSO_2P)	Organic (as FSO + FSO_2)	Solids (as fenamiphos)
Seedlings	4.8 (FSO + FSO_2P)	16.9	1.7
Leaves	8.7	3.5	2.7
Stems	0.6	0.35	0.7
Shells	0.2	0.11	0.3
Beans	0.05	0.19	0.5

Further analysis showed that the 16.9 mg/kg sum of fenamiphos sulfoxide and sulfone concentrated by the seedlings was in a ratio of 73:17. In mature plants, the sum of the two metabolites was 3.5 mg/kg in dry leaves and 0.19 mg/kg in dry beans.

Enzymatic hydrolysis of the water-soluble fractions from seedlings and mature plants released fenamiphos sulfoxide phenol equivalent to 60% and 10% of the recovered radioactivity respectively and fenamiphos sulfone phenol equivalent to 40% and 90%.

In a subsequent crop rotation study on soya beans (Hanna and Schermoly, 1980), ring-labelled [^{13,14}C]fenamiphos was applied to sandy loam soil at a rate equivalent to 6.72 kg ai/ha. Soya beans were planted immediately after treatment and harvested after 30 days (emergency re-plant) and 120 days (immediate rotational crop). Sugar beet, wheat and mustard were planted 31 days after treatment and sugar beet, oats and mustard 115 days after treatment. Soil was analysed at intervals at and after the 31- and 115-day plantings. Crop samples were separated into tops, roots, foliage, stalks, greens and chaff before analysis. The results are shown in Tables 27-29.

Table 27. Total radioactive residues in soil and in crops planted 31 and/or 115 days after soil treatment.

DAT	TRR, mg/kg as fenamiphos, in soil and rotational crops planted after 31 or 115 days									
	Soil		Sugar beet (31)		Sugar beet (115)		Mustard (31)	Mustard (115)	Wheat forage (31)	Oat forage (115)
	30[1]	120[1]	Root	Tops	Root	Tops				
0	3.07	2.98								
31	2.29	2.66								
45		1.99								
59	2.98		13.0				8.53		25.7	
76		1.37								
90		1.70								
115	1.68	1.80	3.60				1.35		3.75	
143	1.62		2.81				0.60		2.56	
185	1.57	1.91	1.12	1.28	0.77		0.42	0.72	1.12	0.91
213		1.43			0.66			0.49		1.09
276		1.90	0.73	0.30	0.47	0.44	0.25	0.36	0.81	0.94
308	1.54	1.88	0.61	0.30	0.44	0.41		0.37		1.67
328	1.64	1.28			0.69	0.19		0.31		
350		1.12								
365 Harvest									3.50 straw	1.91 straw
									0.43 grain	0.63 grain
									2.48 chaff	3.06 chaff

[1]DAT for soya bean harvest

The data show little difference between the TRR in crops planted 30 days and 120 days after treatment. Sugar beet roots differ from tops and from the other plants in that the TRR in the roots is higher in the 31-day than in the 115-day planting at the same intervals after treatment. The data suggest that fenamiphos did not break down rapidly in these conditions.

Table 28. Distribution of radioactivity in extracted fractions of rotational crops.

Crop	Planting, DAT	^{14}C, % of TRR and mg/kg as fenamiphos					
		Organic		Aqueous		Insoluble	
		% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Sugar beet	31	13	0.04	44	0.13	43	0.13
Sugar beet tops	31	13	0.08	78	0.48	9	0.05
Sugar beet	115	16	0.03	50	0.10	34	0.06
Sugar beet tops	115	15	0.10	70	0.48	15	0.11
Mustard	31	23	0.06	68	0.17	9	0.02
	115	25	0.08	65	0.20	10	0.03
Wheat straw	31	30	1.38	31	1.43	39	1.79
Oat straw	115	23	0.86	31	1.16	46	1.72
Oat grain	115	10	0.06	20	0.12	70	0.45

The results are in agreement with those found in plant metabolism studies conducted over prolonged periods: most of the radioactivity is extracted into the aqueous fractions owing to conjugation of the metabolites.

Table 29. Metabolites in organosoluble fractions of extracts of rotational crops.

Crop	Planting, DAT	% of TRR in samples as				$FSO + FSO_2$, as mg/kg as F
		FSO	FSO_2	Phenols	Total (FSO + FSO_2)	
Sugar beet	31	3	4	1	7	0.02
Sugar beet tops	31	2	4	2	6	0.04
Sugar beet	115	5	5	1	10	0.02
Sugar beet tops	115	2	3	4	5	0.03
Mustard	31	4	5	2	9	0.02
	115	5	8	1	13	0.04
Wheat straw	31	4	5	16	9	0.41
Oat straw	115	1	1	6	2	0.07
Oat grain	115	1	1	4	2	0.01

Fenamiphos sulfoxide, fenamiphos sulfone and their phenols were identified as the major radioactive components in the organic fraction.

[1-*phenyl*-^{13,14}C]fenamiphos was applied to sandy loam soil at a rate of 7.6 kg ai/ha (Linke-Ritzer and Brauner, 1990). Rotational crops of silver beet (Swiss chard), red beets and wheat were planted 30, 120 and 269 days after application (three crop rotations). Soya beans were planted in the treated soil as a cover crop and removed 30, 120 and 269 days after treatment to plant the rotational crop. The crops were harvested at maturity, and samples of immature wheat forage were taken in addition to the mature crop. Soil samples were collected 30, 120, 269 and 392 days after application. The results are shown in Tables 30-32.

Table 30. Total radioactivity and identified compounds in soil at intervals after treatment.

Compound or fraction	Residues in soil, % of applied radioactivity at DAT			
	30	120	269	392
Fenamiphos	0.22	0.06	0.01	–
FSO_2	0.43	0.48	0.16	0.14
FSO_2P	0.28	0.46	0.01	0.02
FSOP	0.35	0.14	0.02	0.01
FSO	2.64	1.29	0.24	0.20
Origin	0.05	0.07	0.03	0.02
Bound	0.54	1.26	1.32	1.18
Total	4.51	3.80	1.80	1.60
TRR*	75	63	30	27

* Assuming TRR at day 0 =100%.

The figures clearly show that the total radioactivity in soil decreases with time after application. Similarly, the residues found in the crops show that the radioactivity decreased with each rotation (Table 31).

Table 31. Total radioactive residues in rotational crops.

Crop	TRR, mg/kg fenamiphos equivalents at each rotation		
	Rotation 1 (30 days)	Rotation 2 (120 days)	Rotation 3 (269 days)
Swiss chard	8.71	1.25	0.57
Red beets			
Roots	4.62	0.48	0.10
Tops	7.31	2.83	0.36

Wheat			
Forage	17.30	15.17	2.36
Straw	46.43	19.79	4.78
Kernels	0.98	0.73	0.20

The distribution of radioactivity in the aqueous and organic phases of the crop extracts (Table 32) indicates that in the first rotation the radioactivity is predominantly extracted into the organic phase and at the second and third rotations there is an increase in the extraction into the aqueous phase and in the bound residues.

Table 32. Distribution of radioactivity in extracts of rotational crops (Linke-Ritzer and Brauner, 1990).

Fraction	% of radioactivity in sample					
	Swiss chard	Red Beets		Wheat		
		Roots	Tops	Forage	Straw	Grain
Rotation 1						
Organic	54	29	36	67	34	17
Aqueous	45	51	62	28	56	59
Bound	0	20	3	6	10	24
Rotation 2						
Organic	9	10	17	68	21	7
Aqueous	81	61	73	29	67	25
Bound	10	30	11	3	12	68
Rotation 3						
Organic	15	5	13	75	17	4
Aqueous	74	49	71	16	62	17
Bound	11	46	17	9	21	79

The results are consistent with the formation of phenol conjugates and bound residues as fenamiphos is progressively metabolized.

Table 33. Identification of radioactive residues at each rotation (Linke-Ritzer and Brauner, 1990).

Compound	Radioactivity, % of TRR in sample					
	Swiss chard	Red beets		Wheat		
		Roots	Tops	Forage	Straw	Grain
Rotation 1						
F	0.4	ND	0.4	ND	ND	ND
FSO	28.1	12.4	19.0	31.3	10.4	4.0
FSO_2	20.2	7.3	11.1	18.0	14.1	7.8
FSOP	3.1	4.6	2.1	12.1	5.6	3.8
FSO_2P	4.9	8.1	3.4	10.6	5.8	15.1
OH-FSO_2P	1.2	1.0	0.2	2.4	0.5	11.2
FSOP-glu	2.0	5.5	4.1	3.4	10.3	9.4
FSO_2P-glu	1.0	4.1	3.7	5.2	13.5	15.9
FSO_2P-conj	15.7	7.0	18.0	1.4	1.7	ND
DAFSO	13.9	ND	13.2	2.3	ND	ND
Subtotal	90.5	50.1	75.2	86.7	62.0	67.2
Unidentified	8.9	23.2	14.9	2.2	11.6	3.9
Bound	0.5	20.4	2.5	5.5	9.9	24.2
Rotation 2						
F	ND	ND	ND	ND	ND	ND
FSO	1.4	3.1	7.2	19.1	5.3	1.1
FSO_2	1.8	3.6	6.1	18.6	8.6	2.9
FSOP	0.3	0.4	0.2	10.3	3.3	2.2
FSO_2P	7.2	7.2	3.2	24.6	6.3	4.9

Compound	Radioactivity, % of TRR in sample					
	Swiss chard	Red beets		Wheat		
		Roots	Tops	Forage	Straw	Grain
OH-FSO_2P	1.3	4.6	ND	1.5	0.4	2.6
FSOP-glu	ND	8.8	10.4	0.9	8.1	2.6
FSO_2P-glu	2.5	ND	8.6	2.0	9.4	8.0
FSO_2P-conj	24.7	3.8	14.5	1.6	3.1	2.8
DAFSO	37.3	ND	5.6	3.3	ND	ND
Subtotal	76.5	31.5	55.8	81.9	44.5	27.1
Unidentified	14.0	38.8	14.4	2.5	9.6	5.6
Bound	9.5	29.8	10.7	3.4	11.7	67.7
Rotation 3						
F	0.1	ND	0.1	ND	<0.1	0.1
FSO	4.1	1.7	4.5	26.1	4.5	1.0
FSO_2	5.8	2.1	4.6	29.1	8.5	1.9
FSOP	0.5	ND	0.4	5.8	1.1	0.2
FSO_2P	4.5	2.3	3.0	21.8	2.2	1.5
OH-FSO_2P	ND	1.4	ND	5.0	ND	0.6
FSOP-glu	ND	10.5	6.2	0.5	6.4	ND
FSO_2P-glu	2.8	2.8	10.9	0.5	11.6	5.1
FSO_2P-conj	25.0	7.9	11.5	0.3	3.1	1.9
DAFSO	28.5	ND	ND	ND	ND	1.9
Subtotal	71.3	28.7	41.2	89.1	37.4	14.2
Unidentified	18.0	25.4	42.2	2.0	6.4	5.2
Bound	10.9	45.9	16.7	9.0	20.6	78.6

In general there is an overall decrease in the levels of identified residues with time, although in Swiss chard the levels of the FSO_2P conjugates increase with each rotation. The percentages of bound residues increase with time in all the crops.

Nemacur 3 was sprayed onto soil at three sites at a rate equivalent to 6.72 kg ai/ha and incorporated immediately after application (Pither, 1991). Rotational crops were planted 1, 4 and 8 months after the soil treatment (plant-back period). Representative crops comprised cereals and root and leafy vegetables. All crops were sampled at harvest, and immature forage samples were collected approximately 45 days after planting. Soil core samples (0-15.2 and 15.2-30.5 cm depth) were taken immediately after treatment, at planting and at harvest. Residues in soil were determined on a dry weight basis. The results are shown in Tables 34-36.

Table 34. Fenamiphos residues in cereals planted as rotational crops.

Crop/Sample	Plant-back period, months	Residue, mg/kg		
		Mississippi	Texas	Kansas
Wheat				
forage	1	0.75, 0.88	0.02	
grain		<0.01	NA	
straw		0.18	<0.01	
forage	4		<0.01	
grain			<0.01	
straw			<0.01	
Sorghum				
forage	1			0.05
grain				<0.01
straw				0.03
forage	4	0.44, 0.68		0.01
grain		<0.01		<0.01
straw		0.02		<0.01

Crop/Sample	Plant-back period, months	Residue, mg/kg		
		Mississippi	Texas	Kansas
forage	8	<0.01		
grain		<0.01		
straw		<0.01		

Table 35. Fenamiphos residues in root and leafy vegetables planted as rotational crops.

Crop/Sample	Plant-back period, months	Residue, mg/kg		
		Mississippi	Texas	Kansas
Turnip				
tops	1	0.05	<0.01	0.02
roots		<0.01	<0.01	<0.01
tops	4		<0.01	<0.01
roots			<0.01	<0.01
Spinach leaves	1	0.02		0.10
	4			0.03
Mustard leaves	1		0.03	
	4		<0.01	

Table 36. Fenamiphos residues in soil at intervals before cropping.

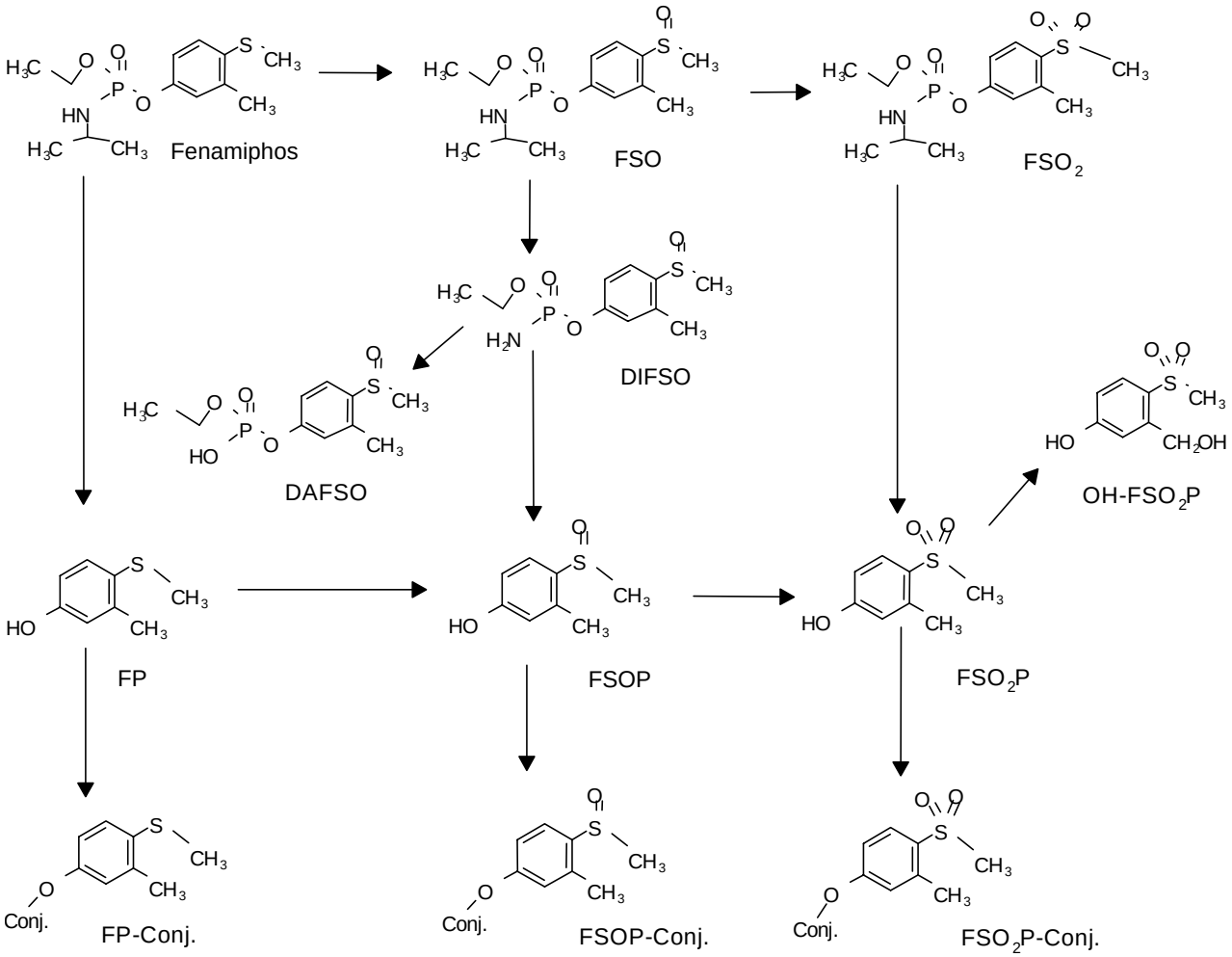
Soil core depth, cm	Plant-back period, months	Residue, mg/kg		
		Mississippi	Texas	Kansas
Cereal plots	1			
0-15.2		0.61	0.15	1.55
15.2-30.5		<0.01	<0.01	<0.01
Leafy plots				
0-15.2		0.73	0.24	0.79
15.2-30.5		<0.01	<0.01	<0.01
Root plot				
0-15.2		1.13	0.33	1.21
15.2-30.5		<0.01	<0.01	<0.01
Cereal plots	4			
0-15.2		0.96	<0.01	0.43
15.2-30.5		0.34	<0.01	0.01
Leafy plot				
0-15.2			<0.01	0.26
15.2-30.5			<0.01	<0.01
Root plot				
0-15.2			<0.01	0.39
15.2-30.5			<0.01	<0.01
Cereal plots	8			
0-15.2		0.56		
15.2-30.5		0.16		

Residues were present in the top core soil samples but were below the limit of detection in most of the lower cores. The results show that there is a correlation between residues in the top layer of the soil and the residues found in cereal forage, turnip tops and leafy vegetables planted 1 and 4 months after treatment.

In summary, the metabolism and crop rotation studies show similar results. After treatment of a crop, or planting in a first rotation after soil treatment, the major transformation of fenamiphos is via formation of the sulfoxide and sulfone, which are both soluble in organic solvents. As the crop matures or is planted in a second rotation, fenamiphos sulfoxide and sulfone are converted to their phenol conjugates after cleavage of the phosphate ester bond. Both phenol conjugates are extractable

in aqueous solvents. The transient metabolites DIFSO and DAFSO were not found in the metabolism studies but DAFSO was isolated in the rotation studies, and both may be envisaged as intermediates formed before the phenols. Proposed transformation pathways are in shown in Figure 2.

Figure 2. Proposed metabolic pathway of fenamiphos in treated and rotational plants.



F	fenamiphos	FSO	fenamiphos sulfoxide
FSO_2	fenamiphos sulfone	DAFSO	desamino-fenamiphos sulfoxide
DIFSO	desisopropyl fenamiphos sulfoxide	FP	fenamiphos phenol
FSOP	fenamiphos sulfoxide phenol	FSO_2P	fenamiphos sulfone phenol
FP-Conj.	fenamiphos phenol conjugate	FSO_2P-Conj.	fenamiphos sulfone phenol conjugate
FSOP-Conj.	fenamiphos sulfoxide phenol conjugate		
OH-FSO_2P	fenamiphos sulfone phenol, hydroxylated at the 3-methyl group		

Environmental fate in soil

Photolysis

Samples of sandy loam soil (0.5 g) were treated with 10 µg [1-*phenyl*-^{14}C]fenamiphos and irradiated for 0, 1, 2, 4, 6, 12, 24 or 48 hours before radioassay (Dime *et al.*, 1983). The samples were extracted with acetone/water and centrifuged, and the supernatant was radioassayed. The radioactive compounds were further characterized by TLC.

The half-life was calculated to be 1.6 hours (k_1 = 0.42 h^{-1}); fenamiphos was stable in the control soil. Approximately 99% of the radioactivity was extracted from both control and irradiated soils, except from the 48-hour sample where the recovery was 90%. The radioactivity during the 48 hours was due to fenamiphos, ranging from 7 to 91%, fenamiphos sulfoxide from 5 to 64%, and fenamiphos sulfone from 0.5 to 6.6% of the TRR.

In a similar study (Hanlon, 1988) [^{13,14}C]fenamiphos was applied to sandy loam soil at a concentration of 9.14 mg/kg. Samples were exposed to natural sunlight for 0, 1, 2, 3 or 4 hours after treatment, and control samples were kept in the dark for similar periods. All samples were extracted with acetonitrile/water and centrifuged, and the supernatant was assayed by liquid scintillation counting. Compounds were identified by HPLC. Extracted radioactivity ranged from 99.6% at 0 hours to 98.2% at 4 hours. The calculated half-life was reported as 2.7 hours, with a first-order rate constant of 0.25 h^{-1}. Fenamiphos accounted for 99.6 to 33.8% of the extracted radioactivity from 0 to 4 hours after treatment and fenamiphos sulfoxide for 34.8% at 1 hour to 64.4% at 4 hours.

In summary, the soil photolysis studies show that fenamiphos is rapidly degraded to fenamiphos sulfoxide according to first-order kinetics, with half-lives of 1.6 hours under laboratory conditions and 2.7 hours in natural sunlight.

Adsorption/desorption

The adsorption and desorption of labelled fenamiphos on sand, sandy loam, silt loam and clay loam was investigated by Daly (1988). Solutions of 250, 187, 125 and 25 µg/ml of [1-*phenyl*-^{14}C]fenamiphos were prepared in 0.01 molar $CaCl_2$ solution. Liquid scintillation counting was used to measure the concentrations of radioactivity in the aqueous solutions, and HPLC to determine the radiochemical purity of the [^{14}C]fenamiphos in the $CaCl_2$ solution at the beginning and end of the test period.

To 3 g samples of each soil were added 10 ml aliquots of each concentration of fenamiphos solution and the suspensions were shaken in darkness for 8 hours at 25°C. The soil suspensions were then centrifuged and the supernatants removed by decantation after the pH had been measured; aliquots were taken for LSC. For the desorption phase, aliquots of 0.01 molar $CaCl_2$ were added to each sample according to the volume removed after the adsorption experiment. The suspensions were shaken in darkness for 24 hours at 25°C, centrifuged, the supernatants removed, and the volumes measured. The wet soil was combusted for radioanalysis and the supernatant taken for liquid scintillation counting.

HPLC analyses of the supernatants from soils treated with the 250 µg/ml solution showed that fenamiphos was stable, with [^{14}C]fenamiphos present at 97.8%, 98%, 97.4% and 97.6% of its initial level in sand, sandy loam, silt loam and clay loam respectively after 8 hours, and recoveries of total ^{14}C from the sand, sandy loam, silt loam and clay loam 99.4%, 102%, 104% and 111% respectively.

The adsorption constants (K_{oc}) and Freundlich constants (K_d, n) were calculated (Table 37).

Table 37. Adsorption and desorption of [^{14}C]fenamiphos (Daly, 1988).

Soil	% Organic C	Adsorption		Desorption	
		K_d	K_{oc}	K_d	K_{oc}
Sand	0.53	2.86	543.4	2.61	496.3
Sandy loam	0.58	0.96	165.6	0.68	117.9
Silt loam	1.53	3.46	226.5	4.29	281.3
Clay loam	1.16	1.98	171.0	1.47	127.1

The mobility of a compound is directly related to its adsorption properties, and K_{oc} is used to rank chemicals with respect to their leaching potential:

K_{oc}	>5000	immobile in soil
	2000-5000	slight mobility
	500-2000	low mobility
	150-500	medium mobility
	50-150	high mobility

From the adsorption K_{oc} values the mobility of fenamiphos is estimated to be low in sand and medium in sandy loam, silt loam and clay loam.

The investigation of the behaviour of fenamiphos in 16 soils from different locations was the subject of a Ph.D. dissertation (Simon, 1990). The degradation of fenamiphos in the soils was investigated, and the adsorption of fenamiphos, fenamiphos phenol sulfoxide and fenamiphos phenol sulfone was measured. The soils and their physicochemical properties are tabulated below.

Table 38. Properties of soils investigated (Simon, 1990).

Location	Clay, %	Silt, %	Sand, %	H_2O capacity	pH ($CaCl_2$)	pH (H_2O)	% organic C
Canada	22.7	47.6	29.7	43.5	6.8	7.27	6.52
Sweden	8.5	9.0	82.5	11.7	6.6	6.33	1.23
Germany/Puch	14.1	74.9	11.0	25.7	6.4	6.98	1.21
Germany/Speyer	4.5	14.1	81.4	18.3	5.1	6.45	2.22
Netherlands	19.3	58.0	22.7	23.3	6.6	6.60	1.60
France	28.1	39.9	32.0	22.8	7.5	7.96	1.58
USA/Indiana	12.0	25.6	62.4	12.1	6.5	6.42	0.95
USA/Nebraska	27.0	69.8	3.2	30.8	5.3	6.68	1.51
Japan/Toyoda	9.8	48.1	42.1	58.3	5.9	5.97	3.53
USA/Florida	1.3	3.3	95.4	5.2	5.8	6.58	0.77
Costa Rica	29.6	41.6	28.8	51.8	4.9	6.03	4.76
Brazil/P. Fundo	44.4	24.4	31.2	23.1	4.8	5.79	1.63
Brazil/Parana	53.5	30.9	15.6	31.3	7.0	6.52	2.28
Thailand	55.3	43.0	1.7	37.0	4.5	5.72	1.63
Phillipines	15.2	42.3	42.5	24.9	5.5	5.83	0.73
Japan/Tsurug.	10.6	47.2	42.2	59.8	5.9	7.10	3.58

The labelled comounds were [1-*phenyl*-$^{13/14}$C]fenamiphos, [1-*phenyl*-^{14}C]fenamiphos phenol, [1-*phenyl*-^{14}C]fenamiphos sulfoxide phenol and [1-*phenyl*-^{14}C]fenamiphos sulfone phenol. Concentrations of 0.5, 1, 2, 5 and 10 mg/l of fenamiphos in 0.01 molar $CaCl_2$ were prepared and 10 ml of each solution was added to 2 g of each soil. The samples were shaken for 4 hours at room temperature, then centrifuged. Aliquots of 0.5 ml of each supernatant were taken for liquid scintillation counting. The experiments with fenamiphos phenol sulfoxide and fenamiphos phenol sulfone were conducted in the same way with concentrations of 0.1, 0.5, 1, 2 and 5 mg/l.

Table 39. Calculated adsoption isotherms, adsorption constants (K_{oc}) and Freundlich constants (K_f).

Soil	Fenamiphos		Fenamiphos sulfoxide phenol		Fenamiphos sulfone phenol	
	K_f	K_{oc}	K_f	K_{oc}	K_f	K_{oc}
Canada	19.42	297.9	6.97	82.6	8.67	133.1
Sweden	3.43	279.7	0.15	12.5	0.61	49.4
Germany/Puch	1.35	111.6	0.35	28.8	0.57	47.2
Germany/Speyer	3.96	178.4	0.99	44.5	1.28	57.7
Netherlands	5.76	380.0	0.66	41.3	1.06	66.1
France	2.52	159.5	0.40	25.7	0.64	40.4
USA/Indiana	2.22	234.7	0.82	86.4	0.98	103.4
USA/Nebraska	4.72	312.6	1.78	118.3	2.31	152.9
Japan/Toyoda	2.69	76.2	0.96	27.2	1.09	31.0
USA/Florida	1.74	226.0	1.01	132.1	1.13	146.8
Costa Rica	17.30	363.4	7.88	165.6	9.83	206.6
Brazil/P. Fundo	2.28	140.5	0.92	56.3	1.11	68.0

Soil	Fenamiphos		Fenamiphos sulfoxide phenol		Fenamiphos sulfone phenol	
	K_f	K_{oc}	K_f	K_{oc}	K_f	K_{oc}
Brazil/Parana	6.02	264.1	2.77	121.7	3.70	162.4
Thailand	23.34	1432	1.67	102.4	3.23	198.5
Phillipines	2.47	339.7	0.33	44.7	0.38	52.0
Japan/Tsurugashima	7.27	205.9	3.89	108.8	4.35	121.5

The soil from Thailand with a high clay and silt content showed the highest adsorption of fenamiphos. The soils from Canada and Costa Rica showed high K_f values for fenamiphos and the two metabolites, with the highest for both metabolites in the Costa Rica soil. In general, the adsorption constants of fenamiphos sulfoxide phenol and fenamiphos sulfone phenol were lower than those of fenamiphos.

The adsorption and desorption of fenamiphos sulfoxide and fenamiphos sulfone on a clay loam from France and a silt loam from The Netherlands was investigated by Fent (1995a,b). The characteristics of the two soils are shown below.

	Netherlands	**France**
Clay	19.3%	28.1%
Silt	58.0%	39.9%
Sand	22.7%	32.0%
Organic C	1.6%	1.58%
pH (H_2O)	6.6	8.0

The soils (12 g) were treated with [^{14}C]fenamiphos sulfoxide and sulfone at concentrations of 5.09, 1.10, 0.20 and 0.04 mg/l in 0.01 M $CaCl_2$ and 0.00018 M biocide and the mixtures shaken for 1, 5, 9, 24, 48, 53 or 72 hours at 22°C. After treatment, the soil mixtures were centrifuged and ^{14}C was determined in the supernatants by liquid scintillation counting and in the soil by LSC after combustion; the purity of the radioactive substances was checked by TLC. To measure desorption the remaining soil from each test was suspended in 0.01 molar $CaCl_2$ and shaken for the same time as for the adsorption measurement. The radioactivity in the supernatant was determnied after centrifugation. The results are shown in Table 40.

Table 40. Adsorption and desorption of fenamiphos sulfoxide and sulfone (Fent, 1995a,b).

Soil	Fenamiphos sulfoxide		Fenamiphos sulfone	
	K_d	K_{oc}	K_d	K_{oc}
Adsorption				
Silt loam (Netherlands)	3.60	225	4.98	311
Clay loam (France)	0.71	44.8	1.04	66
Desorption				
Silt loam	3.10	194	4.58	286
Clay loam	1.12	71.2	1.64	104

The results showed that the proportions of fenamiphos sulfoxide adsorbed to The Netherlands soil were 67.7 to 70.7% of the applied concentration and to the French soil 27% to 36.8%. The corresponding percentages of fenamiphos sulfone adsorbed were 74.3 to 77.3% and 35.2 to 47.1%. Analysis indicated that >96% of the measured radioactivity in both soil supernatants was due to fenamiphos sulfoxide and >99% and 88% of the ^{14}C in the silt and clay loam soils respectively was accounted for by fenamiphos sulfone.

Desorption ranged from 34.5% to 64.3% of the applied concentrations of fenamiphos sulfoxide and 23.4 to 55.7% of the applied concentrations of fenamiphos sulfone.

Mobility. The leaching of aged residues of [1-*phenyl*-^{14}C]fenamiphos incorporated into a sandy laom and a silt loam soil at a concentration equivalent to 10 kg ai/ha was investigated by Spiteller (1987). The soils were weighed into incubation vessels and water added to adjust the moisture content to 40%. The vessels were fitted with traps for $^{14}CO_2$ and other volatiles and stored at 21°C for 15, 30 or 63 days. After ageing, the samples were extracted with acetone/H_2O followed by CH_3Cl/MeOH and centrifuged. The supernatants were analysed by TLC and the unextracted residues by combustion and LSC.

In the leaching experiments, columns of each soil were prepared and saturated with water. The corresponding soil containing the aged residues was added to the top of each column, the columns were watered evenly for 48 hours, and the leachate was collected in fractions. The columns were drained, and the soil was divided into segments and analysed for radioactivity. The leachate fractions were centrifuged and ^{14}C in the supernatant was measured by LSC. Fractions containing more than 1% of the applied radioactivity were worked up further. The extracts were partitioned into CH_3Cl and analysed by TLC.

Table 41. Distribution of residue components in aged soils (Spiteller, 1987).

Compound	^{14}C, % of applied, after ageing period (days)					
	Silt loam			Sand loam		
	0	15	63	0	15	63
F	80.3	8.5	2.6	78.5	23.9	5.0
FSO	6.5	39.6	19.1	5.1	57.3	49.0
FSO_2		24.5	20.8		6.6	16.5
FP						
FSOP			1.0			2.8
FSO_2P		7.8	16.8			6.7
Unidentified	7.5	4.3	6.6	10.6	6.6	4.6

Less than 1% of the applied radioactivity was found in the eluates from the silt soil aged for 0, 15 or 63 days, but 4.3 and 15.9% of the applied radioactivity was recovered in the volatile traps after 15 and 63 days respectively. From the sandy soil, 3.5%, 56.8% and 52.9% of the applied radioactivity was recovered in the eluate fractions after 0, 15 and 63 days ageing respectively.

Table 42. Radioactive compounds in the organic and aqueous fractions from extracts of the leachates, expressed as a percentage of applied radioactivity.

Compound	Organic			Aqueous		
	0 days	15 days	63 days	0 days	15 days	63 days
F						
FSO	2.7	47.9	33.3			0.2
FSO_2		4.7	7.7			0.1
FP						
FSOP					0.2	0.7
FSO_2P						0.2
Unidentified	0.4	2.8	6.2		1.1	1.1

The results show that fenamiphos is transformed mainly into fenamiphos sulfoxide and sulfone. Although fenamiphos phenol was not found, fenamiphos phenol sulfoxide and sulfone were both found after 63 days ageing.

In a subsequent laboratory leaching study (Mulford, 1987a), a sandy loam soil from Kansas was treated with [1-*phenyl*-^{13,14}C]fenamiphos at a rate of 11 mg/kg and incubated for 30 days at 22-24°C under aerobic conditions. The moisture content of the soil was increased to 75% and volatiles were collected in NaOH traps. Sub-samples of the treated soil were analysed for radioactivity by combustion analysis followed by liquid scintillation counting.

The main radioactive compounds in the aged soil were fenamiphos and fenamiphos sulfoxide, accounting for 45.6 and 46.9% of the applied radioactivity respectively. The remaining radioactivity was due to fenamiphos sulfone, fenamiphos phenol sulfoxide and fenamiphos phenol sulfone, contributing 2.3, 2.7% and 1% of the applied radioactivity respectively.

Three soils were used in the leaching study, a Californian sandy loam, sand from Indiana and the Kansas sandy loam. The aged soil treated with fenamiphos was introduced into columns containing the three soils at a rate equivalent to 22.3 kg ai/ha. The samples were stored frozen for 15 days before leaching and prepared by saturating with 0.01 molar $CaCl_2$ solution before adding the aged soil. Each column was then leached continuously for 2 days with 1160 ml of 0.01 molar $CaCl_2$. The leachate was collected in fractions and assayed by liquid scintillation counting. The fractions were combined and extracted with CH_2Cl_2/CH_3CN (2:1). The organic extracts were concentrated and analysed by TLC and HPLC. After leaching the soils were sectioned, dried and assayed by combustion and liquid scintillation counting. The results are shown in Table 43.

Table 43. Properties of three leached soils and distribution of residues in the extracted leachate (Mulford, 1987a).

Properties	Soil		
	California sandy loam	Indiana sand	Kansas sandy loam
% sand	69	90	66
% silt	21	8	32
% clay	10	2	2
% organic C	1.2	0.8	2.4
pH (0.01 molar $CaCl_2$)	5.4	4.3	5.1
CEC (meq/100 g)	12	6	17
Particle density (g/cm^{-3})	2.6	2.6	2.6
	% of applied ^{14}C as		
F	1.0	8.6	0
FSO	40.8	48.8	14.6
FSO_2	2.0	2.5	0.7
FSOP	1.9	2.1	0.3
FSO_2P	0.7	0.8	0
Unidentified	0	0	0.3
Aqueous fraction	0.8	1.0	0.4
Total	47.2	63.8	16.2

The predominant radioactive component in the leachates was fenamiphos sulfoxide, with minor amounts of fenamiphos sulfone and the phenol derivatives. Fenamiphos was present in the Indiana and California soils. The results are in agreement with the study reported by Spiteller.

In the three soils from the leaching experiment, the remaining radioactivity was from fenamiphos and fenamiphos sulfoxide, with the levels decreasing down the column. Overall, the data show that not all of the adsorbed fenamiphos and fenamiphos sulfoxide was leached from the soils.

Degradation

The degradation of [1-*phenyl*-^{14}C]fenamiphos in Florida sand was investigated under aerobic conditions (Lane and Clay, 1989). Soil samples were treated with fenamiphos at 18 mg/kg and mixed thoroughly. The moisture contents were increased to 75% by addition of water. Samples taken immediately after application and after 1, 3, 7, 14, 21, 28, 59, 86 and 120 days were extracted with CH_3CN/H_2O (7:3) at room temperature and the CH_3CN evaporated. The remaining aqueous solution was partitioned with CH_2Cl_2/CH_3CN (2:1), evaporated, and assayed by liquid scintillation counting. The residues were characterized by TLC. The half-life of fenamiphos was calculated to be 30 days.

The results are shown in Table 44. At 120 days after treatment, 7.8% of fenamiphos remained in the soil.

The soil properties are summarized below.

% sand	93
% silt	1
% clay	6
% organic C	1.8
pH	4.9
CEC (meq/100 g in 0.01 molar sodium acetate at pH 8.2)	5
density (g/cm^3)	2.6

Table 44. Residues in Florida sand soil after aerobic degradation (Lane and Clay, 1989).

Compound	% of applied ^{14}C at days after application									
	0	1	3	7	14	21	28	59	86	120
F	97.8	97.8	93.5	82.4	68.4	54.0	47.9	24.5	9.8	7.8
FSO	1.0	3.2	8.3	15.3	24.8	30.2	33.6	35.1	41.4	27.3
FSO_2			0.5	2.0	4.4	9.5	11.9	19.2	21.8	22.3
FSOP				0.7	1.1	1.6	1.7	3.5	2.4	1.5
FSO_2P					0.7	1.1	2.9	11.0	14.1	14.0
H_2O-soluble	0.4	0.3	0.4	0.5	0.3	0.6	0.6	1.2	1.4	1.7
Origin/diffuse	0.7	0.7	0.3	0.2	0.5	0.4	0.3	0.3	0.5	1.2
Solids	0.1	0.6	0.9	1.7	2.1	3.0	3.4	6.9	12.7	17.4
Total	100	102.6	103.9	102.8	102.3	100.4	102.3	101.7	104.1	93.2

Fenamiphos was largely degraded to fenamiphos sulfoxide and fenamiphos sulfone during the 120 days of the study. Fenamiphos phenol sulfone was found at 11 to 14% of the applied radioactivity after 59-120 days. The results are in agreement with those previously found for the degradation of fenamiphos in aged soils.

In a degradation study with a sandy loam soil (Spiteller, 1989a) [1-*phenyl*-$^{13,14}C$]fenamiphos was applied at a rate equivalent to 10 kg ai/ha. The moisture content of the soil was adjusted to 75% and the samples were maintained under aerobic conditions for 6 days with traps for the collection of $^{14}CO_2$. The systems were then made anaerobic by purging with nitrogen and sampled 20, 36, 52 and 66 days after application of the fenamiphos.

The samples were extracted by sonification with acetone/MeOH (1:1) followed by CH_3Cl/MeOH. After each extraction, the samples were centrifuged and the supernatants characterized by TLC and HPLC. The remaining insoluble residues and soil samples were combusted to determine the radioactivity.

The half-life for the anaerobic phase of the study was calculated to be 87.9 days.

Table 45. Residues in treated sandy loam soil after aerobic and anaerobic incubation (Spiteller, 1989a).

Compound	% of applied radioactivity at days after application					
	0	6	20 (14)	36 (30)	52 (46)	66 (60)
F	93.3	36.3	28.6	27.1	23.9	22.2
FSO	3.5	46.5	44.9	39.7	28.8	25.8
FSO_2	<0.1	<0.1	1.1	0.6	0.8	0.9
FP	<0.1	<0.1	0.4	<0.1	4.2	3.2
FSOP	<0.1	2.5	5.8	5.8	3.2	2.6
FSO_2P	<0.1	<0.1	3.5	7.1	10.1	12.8

Unknown	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
Total	96.8	85.3	84.3	80.2	71.0	67.5

Figures in parentheses show days under anaerobic conditions.

The results show that the degradation of fenamiphos is slow under anaerobic conditions. This is not unexpected as the degradation of fenamiphos yields mainly oxidation products. The half-life in the aerobic degradation study of Lane and Clay was reported as 30 days, whereas under anaerobic conditions it was almost 90 days.

In a companion study of aerobic degradation (Spiteller, 1989b), [1-*phenyl*-^{13,14}C]fenamiphos was applied to a sandy loam at a rate equivalent to 10 kg ai/ha and monitored for 365 days. The soil properties are shown below.

% sand	65.5
% silt	26.3
% clay	8.2
% organic C	1.29
pH	6.8
CEC (meq/100 g in 0.01 molar sodium acetate, pH 8.2)	10
density (g/cm^{-3})	2.24

The experimental details were as described above and treated soil samples were analysed 0, 1, 3, 7, 14, 31, 63, 100, 123, 184, 274 and 365 days after application.

The distribution of fenamiphos and its degradation products in the extracted samples at various times is shown in Table 46, which shows that degradation was much faster under aerobic than under anaerobic conditions.

Table 46. Distribution of radioactive residues after aerobic degradation of fenamiphos in sandy loam soil (Spiteller, 1989b).

DAT	% of applied radioactivity									
	F	FSO	FSO_2	FP	FSOP	FSO_2P	FSO_2A	Total	Unextracted	Volatiles
0	90.0	7.6	<0.1	<0.1	<0.1	<0.1	<0.1	97.6	3.4	nd
1	75.8	18.1	<0.1	<0.1	<0.1	<0.1	<0.1	93.9	4.9	<0.1
3	53.8	34.4	0.6	<0.1	1.0	<0.1	<0.1	89.8	9.1	0.1
7	28.5	48.1	2.4	<0.1	2.5	2.1	<0.1	83.6	11.6	0.4
14	13.3	51.4	3.5	<0.1	4.6	6.8	<0.1	79.6	16.2	1.1
31	4.0	36.9	2.3	<0.1	5.4	17.5	0.7	66.8	23.8	4.2
63	1.7	17.7	1.2	<0.1	3.0	24.3	1.9	49.8	38.2	10.5
100	1.1	9.3	0.6	<0.1	2.0	21.3	2.7	37.0	44.3	16.6
123	1.0	7.5	0.2	<0.1	1.5	19.7	3.0	32.9	48.4	19.2
184	0.7	4.0	<0.1	<0.1	1.1	13.9	4.3	24.0	49.4	23.8
274	0.5	1.5	<0.1	<0.1	1.0	7.7	4.3	15.0	51.1	31.8
365	0.4	1.0	<0.1	<0.1	1.1	6.6	4.4	13.5	50.5	34.2

FSO_2A: fenamiphos sulfone anisole

The proportion of extractable radioactivity decreases with time and that of volatile and unextractable materials increases. The results show that the degradation of fenamiphos proceeds via the formation of fenamiphos sulfoxide, followed by fenamiphos sulfoxide phenol and fenamiphos sulfone phenol. Most of the radioactivity after 100 days was unextractable. The main pathways of degradation in soil are oxidation at the methylthio group followed by cleavage of the phosphate bond with the formation of phenol derivatives (Figure 3).

The degradation of fenamiphos was studied in several soils from different geographical locations (Simon, 1990; Simon *et al.*, 1992). The properties and origins of the soils are given in Table 38 above. [1-*phenyl*-$^{13/14}$C]fenamiphos was applied to the soils at a rate equivalent to 10 kg ai/ha (0.77 mg/100 g sample). Control samples were stored in the dark at 22°C, while the test samples were incubated at either 16 and 22°C or 22 and 28°C to represent cool/moderate or subtropical/tropical climates. The samples were incubated for 15, 50 or 90 days.

The extraction procedures included sonication with 1:1 acetone and MeOH followed by 1:1 CH_3Cl and MeOH, centrifugation of each solvent mixture and liquid scintillation counting, with TLC and GC-MS of the organic extracts and combustion analysis of the remaining dry soil samples. The results are shown in Tables 47 and 48 for the cool/moderate climate and subtropical/tropical climate respectively.

Table 47. Aerobic degradation of fenamiphos in nine soils from cool to temperate geographic regions: recovery and distribution of applied radioactivity at 16 and 22°C (Simon *et al.*, 1992)

°C	Days	Radioactivity, % of applied (mean of triplicate samples)										
		Total extracted[1]	F	FSO	FSO_2	FSOP	FSO_2P	FSO_2A	TTR[2]	Un-extracted	$^{14}CO_2$	Recovery
Canada (I)												
22	15	74.5	14.6	45.0	6.2	3.9	4.8	--	65.8	18.5	1.3	94.3
	50	53.5	2.9	24.3	6.3	3.7	14.9	1.4	33.5	36.2	8.3	98.0
	90	45.3	2.2	27.7	4.3	2.7	16.7	2.7	34.2	34.8	17.0	97.1
16	15	79.9	33.5	41.2	2.1	2.1	1.0	--	76.8	14.8	0.6	95.3
	50	70.1	10.0	37.8	7.2	4.8	10.3	--	55.0	21.5	3.4	95.0
	90	54.3	5.3	25.4	4.5	3.4	14.4	1.3	35.2	31.6	10.4	96.3
Sweden (II)												
22	15	85.7	7.8	65.3	9.0	1.3	2.3	--	82.1	6.3	1.7	93.7
	50	70.8	1.5	35.6	19.0	1.1	11.9	1.7	56.1	12.2	8.1	91.1
	90	55.7	0.8	21.0	14.1	0.9	14.8	3.9	35.9	18.5	16.2	90.4
16	15	87.8	18.0	65.7	3.6	0.5	--	--	87.3	3.7	0.6	92.1
	50	81.5	8.6	53.9	11.7	2.1	5.2	--	74.2	8.1	3.1	92.7
	90	77.7	4.9	49.8	14.3	2.0	6.0	0.7	69.0	9.1	4.8	91.6
Germany/Bavaria (III)												
22	15	77.4	2.6	56.6	5.3	2.6	10.3	--	64.5	19.8	4.0	101.2
	50	41.8	0.1	24.1	2.1	0.8	12.3	2.4	26.3	40.3	21.2	103.2
	90	19.2	0.4	7.1	0.5	0.4	7.0	3.3	8.0	48.2	32.9	100.3
16	15	79.8	3.9	66.8	3.0	2.4	3.7	--	73.7	12.7	1.2	93.7
	50	52.6	0.2	29.6	3.1	1.1	17.3	1.3	32.9	23.7	11.3	87.6
	90	33.9	0.5	12.6	1.2	0.4	17.0	1.7	14.3	35.1	21.0	90.0
Germany/Rheinland Pfalz (IV)												
22	15	84.5	15.7	52.3	4.3	7.6	4.1	--	72.3	10.1	2.0	96.6
	50	68.4	2.3	34.9	5.9	11.1	12.3	1.2	43.1	19.8	8.7	96.9
	90	57.7	0.8	23.4	5.2	10.1	16.2	2.0	29.4	25.4	13.2	96.3
16	15	86.5	24.0	54.2	2.5	4.2	0.9	--	80.7	8.5	0.1	95.1
	50	74.9	4.4	44.0	7.4	9.1	8.9	0.5	55.8	13.6	4.1	92.6
	90	66.6	1.7	28.7	7.3	8.1	18.4	1.7	37.7	20.6	9.0	96.2
Netherlands (V)												
22	15	89.3	2.6	68.1	9.6	1.1	7.9	--	80.3	12.7	3.4	105.4
	50	49.4	0.3	24.3	5.7	0.7	14.9	3.1	30.3	29.5	21.8	100.7
	90	22.0	0.5	10.8	2.2	0.4	5.2	2.9	13.5	33.8	39.0	94.8
16	15	90.1	5.1	79.1	3.9	--	2.0	--	88.1	9.0	1.1	100.2
	50	72.5	1.7	37.8	11.6	1.2	19.0	1.2	51.1	18.3	7.8	98.6
	90	42.7	--	18.7	4.7	--	15.8	3.5	23.4	28.6	23.4	94.7
France (VI)												
22	15	65.3	5.5	36.8	1.8	5.4	14.2	0.8	44.1	29.8	2.5	97.6
	50	23.1	1.1	4.8	0.3	0.8	12.2	3.3	6.2	69.1	16.8	109.0

°C	Days	Radioactivity, % of applied (mean of triplicate samples)										
		Total extracted[1]	F	FSO	FSO_2	FSOP	FSO_2P	FSO_2A	TTR[2]	Un-extracted	$^{14}CO_2$	Recovery
	90	10.5	0.6	1.5	0.2	0.2	2.9	3.7	2.3	61.8	32.2	05.5
16	15	79.4	6.8	52.9	0.9	4.4	14.4	--	60.6	23.3	1.6	104.3
	50	52.2	3.8	27.7	0.8	2.8	16.0	1.1	32.3	42.5	7.2	101.9
	90	47.3	3.9	22.4	0.6	2.8	15.2	1.5	26.9	46.4	9.8	104.0
USA/Indiana (VII)												
22	15	79.2	7.3	47.3	6.4	3.7	14.5	--	61.0	18.4	1.5	99.1
	50	56.6	1.3	25.5	6.6	2.1	19.5	1.6	33.4	29.1	7.7	93.4
	90	45.9	1.1	12.5	2.5	1.8	24.7	3.3	16.1	33.8	14.0	93.7
16	15	90.8	24.7	58.6	2.6	2.3	2.6	--	85.9	11.7	0.8	103.3
	50	77.8	13.1	48.7	4.8	3.2	8.0	--	66.6	19.6	2.8	100.2
	90	72.6	4.4	45.5	5.4	4.3	12.3	0.7	55.3	25.9	4.1	102.6
USA/Nebraska (VIII)												
22	15	70.7	6.1	58.1	5.5	1.0	--	--	69.7	13.1	1.0	84.8
	50	67.9	2.1	33.8	22.6	1.6	7.1	0.7	58.5	23.5	6.6	98.0
	90	58.0	0.8	23.4	19.2	1.4	11.5	1.7	43.4	26.3	12.8	97.1
16	15	79.4	12.3	65.5	1.6	--	--	--	79.4	13.0	0.4	92.8
	50	70.9	3.8	54.3	11.4	0.8	0.6	--	69.5	14.9	1.7	87.5
	90	71.0	2.2	37.8	22.8	1.8	6.4	--	62.8	18.9	4.8	94.7
Japan/Toyoda (IX)												
22	15	82.9	48.5	34.4	--	--	--	--	82.9	17.5	0.1	100.5
	50	76.7	17.6	48.9	7.1	2.0	1.1	--	73.6	25.6	0.3	102.6
	90	73.4	7.3	45.6	13.9	2.8	4.1	--	66.8	35.5	1.1	110.0
16	15	86.9	69.1	17.8	--	--	--	--	86.9	10.4	--	97.3
	50	85.2	34.7	48.8	0.6	1.1	--	--	84.1	19.0	0.1	104.3
	90	80.3	24.8	49.3	3.1	2.5	0.6	--	77.2	23.9	0.4	104.6

[1] Including polar products (1%)
[2] Total toxic residues (F + FSO + FSO_2)
-- not detected

F fenamiphos
FSO fenamiphos sulfoxide
FSO_2 fenamiphos sulfone
FSOP fenamiphos sulfoxide phenol
FSO_2P fenamiphos sulfone phenol
FSO_2A fenamiphos sulfone anisole

Table 48. Aerobic degradation of fenamiphos in seven soils from subtropical and tropical geographic regions: recovery and distribution of applied radioactivity at 22 and 28°C (Simon *et al.*, 1992)

°C	Days	Radioactivity, % of applied (mean of triplicate samples)										
		Total extracted[1]	F	FSO	FSO_2	FSOP	FSO_2P	FSO_2A	TTR[2]	Un-extracted	$^{14}CO_2$	Recovery
USA/Florida (X)												
22	15	74.5	30.7	34.4	8.1	1.3	--	--	73.2	10.0	0.6	85.1
	50	60.2	7.6	30.7	15.5	2.0	4.4	--	53.8	22.7	2.7	85.6
	90	52.7	6.7	20.2	16.3	1.8	6.9	0.5	43.2	24.8	4.8	82.3
28	15	69.6	16.5	38.1	11.4	1.7	1.9	--	66.0	14.3	1.2	85.1
	50	51.3	5.3	21.0	16.2	1.8	6.2	0.5	42.5	24.3	5.2	80.8
	90	43.7	2.9	16.4	13.4	2.0	7.6	1.0	32.7	36.3	8.6	88.6
Costa Rica (XI)												
22	15	73.0	15.5	45.4	5.9	3.7	2.5	--	66.8	21.6	2.0	96.6
	50	55.8	5.9	28.9	7.0	5.2	8.2	0.6	41.8	37.1	7.5	100.4
	90	47.5	3.5	21.3	5.5	5.4	10.5	1.3	30.3	39.6	12.0	99.1
28	15	66.9	14.0	37.1	5.2	6.5	4.1	--	56.3	28.9	4.4	100.2
	50	43.2	4.6	20.9	3.6	6.3	6.8	1.0	29.1	47.3	12.4	102.9
	90	36.8	2.6	17.6	3.9	5.0	6.2	1.5	24.1	39.3	16.1	92.2
Brazil/P. Fundo (XII)												
22	15	81.1	11.2	53.5	6.7	5.4	4.3	--	71.4	18.1	2.7	101.0

°C	Days	Radioactivity, % of applied (mean of triplicate samples)										
		Total extracted[1]	F	FSO	FSO_2	FSOP	FSO_2P	FSO_2A	TTR[2]	Un-extracted	$^{14}CO_2$	Reco-very
	50	58.8	2.0	26.2	9.7	5.5	13.5	1.9	37.9	33.4	13.3	105.5
	90	44.3	1.2	13.0	3.5	4.2	18.9	3.5	17.7	32.1	20.8	97.2
28	15	74.5	4.0	49.6	9.2	5.9	5.8	--	62.8	21.4	5.0	100.9
	50	42.6	1.7	15.2	3.7	3.9	14.6	3.5	20.6	33.3	22.4	98.3
	90	23.3	0.7	5.8	1.0	2.4	8.4	5.0	7.5	46.4	36.5	106.2
Brazil/Parana (XIII)												
22	15	71.6	16.9	40.6	5.2	4.5	4.4	--	62.7	28.2	1.1	99.9
	50	49.2	5.1	17.6	5.2	3.8	16.6	0.9	27.9	39.4	9.4	98.0
	90	32.4	2.2	7.8	2.0	2.7	15.6	2.1	12.0	48.5	18.1	99.0
28	15	63.7	11.0	32.3	6.9	5.1	8.4	--	50.2	35.7	3.8	103.2
	50	33.7	2.7	10.6	2.1	2.9	13.3	2.1	15.4	50.5	19.0	103.2
	90	18.2	1.1	4.3	0.9	1.3	8.0	2.6	6.3	52.3	33.7	104.2
Thailand (XIV)												
22	15	86.9	24.6	60.9	0.3	1.1	--	--	85.8	13.8	0.4	101.1
	50	74.3	5.0	52.5	7.7	5.2	3.9	--	65.2	20.6	3.0	97.9
	90	61.2	2.0	39.6	8.5	6.2	4.0	--	51.0	24.6	4.3	90.1
28	15	94.2	25.0	64.2	2.5	2.5	--	--	91.7	16.1	0.6	110.9
	50	70.3	3.7	45.6	11.5	4.9	4.6	--	60.8	27.1	4.4	101.8
	90	50.1	1.9	28.0	9.7	4.2	6.3	--	39.6	30.7	9.9	90.7
Philippines (XV)												
22	15	75.4	6.4	61.7	4.4	1.6	1.3	--	72.5	11.5	1.8	88.6
	50	56.8	1.2	31.7	10.6	1.7	9.6	1.4	43.5	27.0	11.2	95.0
	90	37.7	0.3	18.0	6.7	0.9	9.3	2.1	25.0	35.7	24.2	97.6
28	15	73.4	3.5	57.2	7.5	2.2	3.0	--	68.2	18.3	4.6	96.3
	50	38.8	0.4	22.5	6.4	0.9	5.6	2.5	29.3	30.8	23.3	92.9
	90	19.9	0.2	11.1	2.8	0.6	1.8	3.0	14.1	39.7	40.0	99.6
Japan/Tsurug (XVI)												
22	15	73.4	14.8	56.6	1.1	0.9	--	--	72.5	20.0	0.3	93.7
	50	66.2	4.8	45.1	9.3	3.1	3.9	--	59.2	25.4	1.2	92.8
	90	58.7	1.9	33.7	11.3	3.2	8.0	0.6	46.9	33.2	3.5	95.4
28	15	64.0	5.6	51.0	4.0	2.3	1.1	--	60.6	31.4	0.5	95.9
	50	51.3	2.3	29.3	9.5	2.7	6.7	0.8	41.1	32.8	4.4	88.5
	90	43.7	1.2	22.0	6.6	3.3	8.5	2.1	29.8	44.8	9.9	98.4

[1] Including polar products (1%)
[2] Total toxic residues (F + FSO + FSO_2)
-- not detected

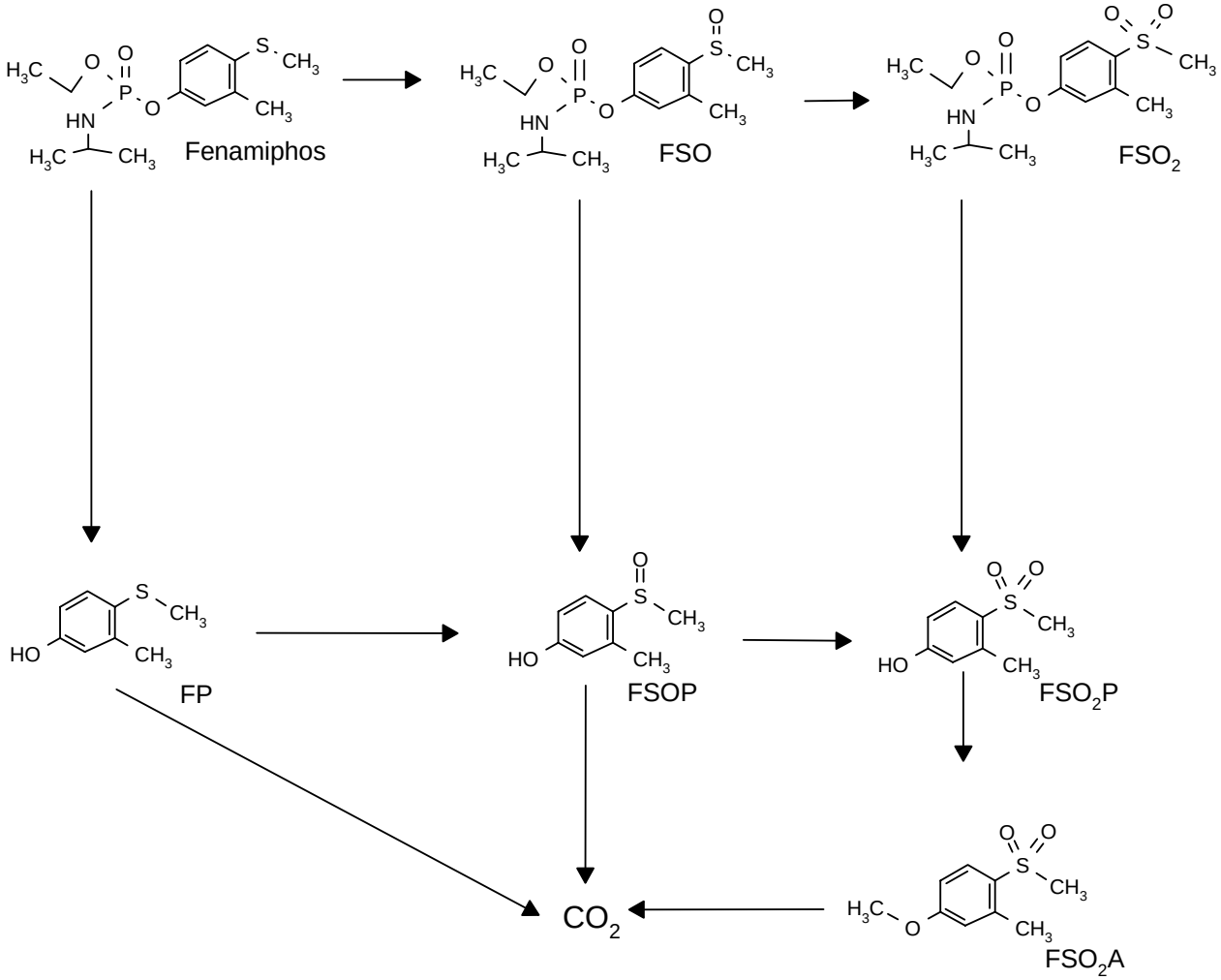
F fenamiphos
FSO fenamiphos sulfoxide
FSO_2 fenamiphos sulfone
FSOP fenamiphos sulfoxide phenol
FSO_2P fenamiphos sulfone phenol
FSO_2A fenamiphos sulfone anisole

From the results, the half-life of fenamiphos was less than 15 days at 22°C in all the soils. If the residues of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone are combined, as all three compounds show nematicidal activity, residues are still detectable after 90 days at 22°C, at levels ranging from 2.3% of the applied radioactivity (France) to 66.8% (Japan/Toyoda). After 50 days in many soils, the proportion of fenamiphos sulfone phenol increased as corresponding levels of fenamiphos sulfoxide and sulfone decreased. The results are in agreement with those of previous studies, as the major degradation products are fenamiphos sulfoxide and fenamiphos sulfone which are then converted to the corresponding phenols by cleavage of the phosphate ester bond. The degradation pathways of fenamiphos in soils are shown in Figure 3.

The half-lives of fenamiphos and/or the sum of fenamiphos and fenamiphos sulfoxide in the studies by Simon (1990), Simon *et al.* (1992), Spiteller (1989a,b) and Lane and Clay (1989) are shown in Table 49.

Fenamiphos was rapidly degraded under aerobic conditions with half-lives of ≤30 days in two experiments. Half-lives of the sum of fenamiphos and fenamiphos sulfoxide (both compounds nematicidal) ranged from 12 to 166 days, depending upon soil type and incubation temperature.

Figure 3. Proposed degradation pathways of fenamiphos in soil under aerobic and anaerobic conditions.



FSO	fenamiphos sulfoxide	FSO_2	fenamiphos sulfone
FP	fenamiphos phenol	FSOP	fenamiphos sulfoxide phenol
FSO_2P	fenamiphos sulfone phenol	FSO_2A	fenamiphos sulfone anisole

Table 49. Half-lives of the sum of fenamiphos and fenamiphos sulfoxide calculated according to first-order kinetics from experiments under aerobic laboratory conditions

Soil and conditions		Application rate, ai	Half-life, days,F + FSO	Reference
Aerobic				
sand	(USA)	18 mg/kg	153 *	Lane and Clay, 1989
sandy loam	(USA)	10 kg/ha	--	Spiteller, 1989b

Soil and conditions		Application rate, ai	Half-life, days,F + FSO	Reference
silty sand loam	(Canada)	10 kg/ha	49/27 **	Simon, 1990
loamy sand	(Sweden)	10 kg/ha	85/37 **	
loamy silt	(Germany)	10 kg/ha	30/23 **	
silty sand	(Germany)	10 kg/ha	50/36 **	
clay silt	(Netherlands)	10 kg/ha	40/27 **	
clay loam	(France)	10 kg/ha	29/12 **	
loamy sand	(USA)	10 kg/ha	81/28 **	
silty loam sand	(USA)	10 kg/ha	68/36 **	
silty loam sand	(Japan)	10 kg/ha	166/86 **	
sand	(USA)	10 kg/ha	35/25 ***	
clay loam	(Costa Rica)	10 kg/ha	32/24 ***	
sandy clay loam	(Brazil)	10 kg/ha	26/18 ***	
silty clay	(Brazil)	10 kg/ha	21/14 ***	
silty clay	(Thailand)	10 kg/ha	70/52 ***	
silty sand loam	(Philippines)	10 kg/ha	33/23 ***	
loamy sand	(Japan)	10 kg/ha	48/28 ***	

[1] Not calculated owing to rapid degradation
* F+FSO+FSO_2
** 1st value at 16°C, 2nd value at 22°C
*** 1st value at 22°C, 2nd value at 28°C

F fenamiphos
FSO fenamiphos sulfoxide
FSO_2 fenamiphos sulfone

In a US study (Kasper and Shadrick, 1993), the half-life of fenamiphos was determined in soils at two sites in California. At Chualar and Fresno, soils placed in vessels located in outdoor plots were treated with [U-*phenyl*-^{14}C]fenamiphos at a rate equivalent to 10.9 kg ai/ha and sampled 6 and 12 hours and 1, 2, 4, 7, 10, 18, 30 and 60 days after treatment. At each sampling the top 3 cm layer of soil was homogenized, extracted and analysed by TLC. Extraction procedures were similar to those used in other studies.

The properties of the soils from the two sites are shown below.

	Fresno soil	**Chualar soil**
% sand	64.7	70.0
% silt	31.3	18.0
% clay	4.0	12.0
% organic C	0.5	1.3
pH	7.5	6.4
CEC (meq/100 g)	6.9	17.3
Density (g/cm^3)	1.41	1.32

The calculated half-lives were 19.9 and 18.2 days in the Fresno and Chualar soils respectively. These values compare well with the 15.7 days reported by Spiteller. Fenamiphos sulfone phenol was the product of interest in this study and it was not detected until day 7. Its levels ranged from 0.4-1.9% and 0.3-3.5% of the applied radioactivity from days 7 to 60 in the Fresno and Chualar soils respectively. The main components of the radioactive residue were fenamiphos, fenamiphos sulfoxide and fenamiphos sulfoxide phenol.

In an earlier study also at sites in Fresno and Chualar (Grace *et al.*, 1990), fenamiphos was applied twice to soil at a rate equivalent to 11.2 kg ai/ha; the treatment interval was 6 months. Half-lives of 16.2 days at Chualar and 17 days at Fresno were reported. These values are in good agreement with previously reported half-lives of fenamiphos ranging from 15 to 30 days. Total residues of the compounds showing nematicidal activity (fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone) were below the limit of determination of 0.01 mg/kg at depths below 61 cm at all

sampling times after a single application. The data from both sites showed that under conditions of field use fenamiphos residues would not readily reach depths greater than 90 cm before dissipation.

In a field dissipation study in North Carolina (Halarnkar *et al.*, 1996), two sprays of fenamiphos were applied to soil at a rate equivalent to 12.3 kg ai/ha, at an interval of 3 months. Soil core samples were taken immediately before and 2 hours after the first application, then 1, 3, 5, 10, 12, 30, 60 and 90 days after the first spray, then 3 hours and 1, 3, 5, 10, 14, 28, 61, 88, 180, 276, 361, 452 and 561 days after the second application. Soil cores were also collected within 21 days after significant rainfall (>7.5 cm in 24 hours). Cores were a minimum depth of 15.2 cm, but not more than 122 cm. Untreated controls were collected within 2 hours after the first spray and 88, 276 and 561 days after the second spray. The treated plots were irrigated and the total rainfall plus irrigation was 145% of the 10-year average rainfall for the study period.

At each sampling the cores were sub-sampled to depths of 0-15.2, 15.2-30.5, 30.5-61, 61-76.2, 76.2-91.4 and 91.4-122 cm. All soil cores down to depths of 61 cm were extracted and analysed by GLC and reversed phase, ion-pair and normal HPLC. The limits of detection by HPLC were 0.01 μg/g for fenamiphos, FSO, FSO_2, FSOP, FSO_2P and FSO_3HP (fenamiphos sulfonic acid phenol). As the soil samples were held in frozen storage for a maximum of 842 days before analysis frozen storage stability studies were also conducted.

The properties of the soil used in the study at depths from which cores were routinely analysed are shown below.

	Core depth (cm)		
	0-15.2 cm	**15.2-30.5**	**30.5-61**
% organic C	0.49	0.38	0.16
pH	6.6	5.5	5.4
CEC	1.02	1.30	0.84
density (g/cm^3)	1.66	1.66	1.68
% moisture (0.33 bar)	3.02	3.01	3.47
% sand	89.2	89.2	85.2
% silt	6.4	6.4	8.4
% clay	4.4	4.4	6.4
Class	sand	sand	loamy sand

The half-life of fenamiphos was determined to be 15.9 days with a first-order rate constant of -0.0437. The half-life is similar to those found in other laboratory degradation studies (15-30 days). The results are shown in Table 50.

Table 50. Distribution of residues after two spray applications of fenamiphos (Halarnkar *et al.*, 1996).

Compound	Maximum residue, mg/kg, at (DAT1)	Dissipation, minimum mg/kg, at (DAT1)	Maximum residue, mg/kg, at (DAT2)	Dissipation, minimum mg/kg, at (DAT2)
F	2.70 (0)	<0.01 (60) all depths	2.52 (0)	<0.01 (180) all depths
FSO	4.10 (3)	0.13 (90)	1.95 (3)	<0.01 (361) all depths
FSO_2	0.44 (12)	<0.01 (90) all depths	0.10 (5)	<0.01 (61) all depths
FSOP	0.13 (30)	0.02 (90)	0.41 (14)	<0.01 (61) all depths
FSO_2P	0.23 (30)	0.03 (90)	0.13 (14)	<0.01 (28) all depths
Total F equivalents	4.68 (3)	0.28 (90)	4.03 (3)	<0.01 (361)

DAT1: days after first spray
DAT2: days after second spray

Recoveries of fenamiphos, fenamiphos sulfoxide, fenamiphos sulfone, fenamiphos sulfoxide phenol, fenamiphos sulfone phenol and fenamiphos sulfonic acid phenol were determined at a level of 1 mg/kg of each compound in fortified field samples. The recoveries were 82-108%, 68-128%, 75-

117%, 69-91%, 78-103% and 72-95% respectively. In a storage stability study samples spiked with fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone were stored for 365 days, when 86, 100 and 100% of the three compounds remained respectively. In another stability study samples of sandy loam soil fortified with fenamiphos sulfoxide phenol, fenamiphos sulfone phenol and fenamiphos sulfonic acid phenol were stored for 731 days. The recoveries were 89, 84 and 95% respectively.

In a similar dissipation study in California (Antle *et al.,* 1996), a sandy loam soil was treated with two sprays of fenamiphos at a rate of 12.3 kg ai/ha, with an interval of 93 days between applications. Soil core samples were taken immediately before and 1, 3, 5, 10, 14, 28, 60 and 93 days after the first application, then 1, 3, 5, 9, 14, 28, 61, 90, 182, 274, 365, 454 and 548 days after the second application. The core depths were as in the previous study.

The soil characteristics are shown below.

		Core depth	
	0-15.2 cm	**15.2-30.5**	**30.5-61**
% organic C	0.22	0.33	0.27
pH	8.1	7.5	7.0
CEC	5.18	4.79	4.97
density (g/cm^3)	1.63	1.57	1.59
% moisture (0.33 bar)	10.77	10.94	9.62
% sand	63.2	61.2	63.2
% silt	28.0	30.0	28.0
% clay	8.8	8.8	8.8
Class	sandy loam	sandy loam	sandy loam

Table 51. Distribution of residues after two spray applications of fenamiphos (Antle *et al.,* 1996).

Compound	Maximum residue, mg/kg, at (DAT1)	Dissipation, minimum mg/kg, at (DAT1)	Maximum residue, mg/kg, at (DAT2)	Dissipation, minimum mg/kg, at (DAT2)
F	1.47 (3)	<0.01 (93) all depths	2.03 (1)	<0.01 (28) all depths
FSO	3.28 (10)	0.08 (93) all depths	2.52 (3)	<0.01 (454) all depths
FSO_2	0.44 (28)	<0.01 (93) all depths	0.09 (3)	<0.01 (9) all depths
FSOP	0.34 (28)	0.02 (93)	0.38 (5)	<0.01 (9) all depths
FSO_2P	0.29 (28)	0.05 93)	0.07 (1, 5)	<0.01 (9) all depths
FSO_3HP			0.14 (182)	<0.01 (548)
Total F equivalents	4.44 (10)	0.26 93)	4.31 (3)	<0.01 (548)

Recoveries at a fortification level of 0.1 mg/kg were 63-95% for fenamiphos, 79-129% for fenamiphos sulfoxide, 82-108% for fenamiphos sulfone, 81-117% for fenamiphos sulfoxide phenol, 89-101% for fenamiphos sulfone phenol and 86-113% for fenamiphos sulfonic acid phenol.

A half-life of 15 days was calculated from samples taken between the first and second applications. This is in agreement with the results of other field degradation studies (Table 52).

Table 52. Half-lives of fenamiphos in various field studies.

Location	Application rate, kg ai/ha	Half-life, days	Reference
Chualar, California	11.2	16.2	Grace *et al*., 1990
Fresno, California	11.2	17.0	
Fresno, California	12.3	15.0	Antle *et al*., 1996
North Carolina	12.3	15.9	Halarnkar *et al*., 1996

Summary of results of soil studies

In laboratory experiments fenamiphos was degraded rapidly under aerobic conditions with half-lives less than 30 days, and more rapidly in sunlight on soil surfaces under laboratory and natural conditions with half-lives of 1.6 and 2.7 hours respectively. Adsorption studies with a variety of soils from cold and tropical regions showed that the adsorption of fenamiphos was dependent upon the clay and silt content. In several degradation studies, fenamiphos was shown to be converted to fenamiphos sulfoxide and sulfone with subsequent transformation to the phenol derivatives.

Hydrolysis

The hydrolysis of [1-*phenyl*-^{14}C]fenamiphos was examined in aqueous buffer solutions (pH 3, 7 and 9) for 30 days at concentrations of 1 and 10 mg/l and temperatures of 30° and 50°C (McNamara and Wilson, 1979). Samples were taken at regular intervals up to 30 days. Each solution was radioassayed and extracted with CH_2Cl_2. The organic fractions from each sample were radioassayed, concentrated, radioassayed again and analysed by TLC. Aqueous fractions from the first extraction which showed much radioactivity were treated with NaCl and HCl before re-extraction with CH_3Cl.

At 30°C more than 95% of the applied radioactivity was extracted into CH_3Cl at pH 7 and 9 at at both concentrations, but at pH 3 the extractable radioactivity decreased from 99% at day 0 to 10% at day 30. After incubation at 50°C for 30 days the extractable radioactivity was 4% at pH 3, 97% at pH 7 and 57% at pH 9 at 1 mg/l, and 6% at pH 3, 97% at pH 7 and 67% at pH 9 at 10 mg/l.

Table 53. Rate constants and half-lives for hydrolysis of fenamiphos in buffer solutions.

pH	°C	Concentration, mg/l	k_1,days $^{-1}$	Half-life, days
3	30	1	0.079	8.8
		10	0.066	10
3	50	1	0.211	3.3
		10	0.232	3.0
9	30	1	0.003	220
		10	0.003	230
9	50	1	0.032	22
		10	0.030	23

The main hydrolysis products at pH 9 at a concentration of 10 mg/l were fenamiphos phenol, fenamiphos sulfoxide phenol and fenamiphos sulfoxide, formed by phosphate ester hydrolysis in basic solution and oxidation at the methylthio group. In pH 3 buffer the major hydrolysis product (50% of the initial radioactivity) was deaminated fenamiphos, with fenamiphos phenol and deaminated fenamiphos sulfoxide accounting for less than 10%.

The hydrolytic degradation of fenamiphos was investigated in buffer solutions at pH 4, 7 and 9 and temperatures of 60, 70 and 80°C by Andersen (1985b) at a concentration of 0.05 molar fenamiphos. The solutions were sealed and incubated in darkness. The concentration of fenamiphos was determined by HPLC.

Table 54. Half-lives and hydrolysis rate constants for degradation of fenamiphos in buffer solutions (Andersen, 1985b).

pH	°C	Hydrolysis constant, k	Half-life
4	60	0.071 day^{-1}	9.8 days
	70	0.217 day^{-1}	3.2 days
	80	0.408 day^{-1}	1.7 days
7	60	0.010 day^{-1}	67.1 days
	70	0.019 day^{-1}	37.2 days
	80	0.050 day^{-1}	13.8 days

pH	°C	Hydrolysis constant, k	Half-life
9	60	0.010 h^{-1}	70 h
	70	0.034 h^{-1}	20.5 h
	80	0.133 h^{-1}	5.2 h

The results show that the hydrolysis of fenamiphos is accelerated by elevated temperatures and is most rapid at pH 9.

The stability of [1-*phenyl*-^{13,14}C]fenamiphos in buffer solutions at pH 5, 7 and 9 in the dark and under sterile conditions was investigated by Mulford (1987b). The labelled fenamiphos was dissolved in sterile acetate, phosphate or borate buffer and assayed for soluble radioactivity. The solutions were sealed in vials, kept in the dark, and analysed 0, 5, 10, 14, 18, 24 and 31 days after preparation. At each sampling the total radioactivity was assayed by liquid scintillation counting and fenamiphos and the hydrolysis products were quantified by HPLC. Each sample was extracted with dichloromethane and analysed by TLC. The recovered radioactivity ranged from 93 to 99%, 94.4 to 96.5% and 98.3 to 100% at pH 5, 7 and 9 respectively. The distribution of the radioactivity is shown in Table 55.

Table 55. Distribution of radioactive compounds in buffered solutions in the dark (Mulford, 1987b).

PH, compound	% of recovered radioactivity at days after application						
	0	5	10	14	18	24	31
pH 5							
F	99.3	97.3	95.4	97.4	97.2	93.4	89.6
FSO	0.1	1.8	4.5	1.9	2.3	6.3	9.9
pH 7							
F	99.6	99.0	96.8	97.6	97.4	95.4	91.9
FSO	0.2	0.6	2.2	1.8	1.7	4.6	8.1
pH 9							
F	99.5	98.4	96.8	96.4	96.1	93.7	90.1
FSO	0.3	0.5	1.7	1.6	1.6	2.5	4.1
FP	0	0.8	1.3	1.7	2.1	3.4	5.2

Fenamiphos sulfoxide was the major hydrolysis product, but fenamiphos phenol was also formed at pH 9. At all sampling times the products accounted for less than 10% of the recovered radioactivity, indicating that fenamiphos is stable in sterile solutions in the dark.

The calculated half-life values are shown in Table 56.

Table 56. Half-lives calculated for fenamiphos in sterile buffer solutions in the dark (Mulford, 1987).

pH	°C	Concentration, mg/l	Rate constant, $days^{-1}$	Half-life, days
5	25	34.5	2.81×10^{-3}	245
7	25	34.0	2.30×10^{-3}	301
9	25	35.4	2.95×10^{-3}	235

The half-lives found in the studies described are compared in Table 57 .

Table 57. Half-lives of fenamiphos found in hydrolysis studies.

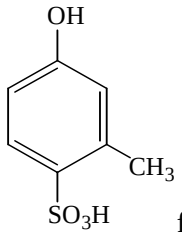
pH	°C	Fenamiphos concentration, mg/l, and label	Half-life, days	Reference
3	30	1 [1-*phenyl*-^{14}C] 10	8.8 10	McNamara and Wilson, 1979, revised 1981
3	50	1 [1-*phenyl*-^{14}C] 10	3.3 3.0	
9	30	1 [1-*phenyl*-^{14}C]	220	

pH	°C	Fenamiphos concentration, mg/l, and label	Half-life, days	Reference
		10	230	
9	50	1 [1-*phenyl*-^{14}C]	22	
		10	23	
4	60	7.5 unlabelled	9.8	Anderson, 1985
	70		3.2	
	80		1.7	
7	60	7.5 unlabelled	67.1	
	70		37.2	
	80		13.8	
9	60	7.5 unlabelled	2.9	
	70		0.9	
	80		0.2	
5	25	34.5 [1-*phenyl*-^{14}C]	245	Mulford, 1987
7	25	34.0 [1-*phenyl*-^{14}C]	301	
9	25	35.0 [1-*phenyl*-^{14}C]	235	

Photolysis

Aliquots of a 12 mg/l solution of [1-*phenyl*-^{14}C]fenamiphos in phosphate buffer were irradiated with a mercury lamp at 27-28°C for 0, 1, 2, 4, 6, 12 or 24 hours (Dime *et al.*, 1983). Controls were kept in the dark. The aqueous solutions were extracted with CH_3Cl and both organic and aqueous phases were radioassayed. TLC was used to identify the radioactive components.

The half-life was 3.6 hours with a first-order rate constant of 0.19 h^{-1}; fenamiphos was shown to be stable under similar conditions in the absence of light. The light intensity was compared to that of a July day in Kansas, and it was reported that the half-life under Kansas light intensity would be 6.8 hours. Recoveries of radioactivity were 94% from the irradiated samples and 99% from the controls. TLC of the organosoluble fractions showed that 34 to >99% of the radioactivity was present in the organic phase and was largely due to fenamiphos, ranging from 94 to 4.3% from 0 to 24 hours of irradiation, and fenamiphos sulfoxide ranging from 4 to 17.3 % over the same period. The water-soluble fractions contained 0.3 to 56.4% of the radioactivity with fenamiphos phenol sulfonic acid (4-hydroxy-2-methylbenzenesulfonic acid), the major component, accounting for 2.3 to 18.6% of the recovered radioactivity. The results are shown in Table 58.



fenamiphos phenol sulfonic acid
(4-hydroxy-2-methylbenzenesulfonic acid)

Table 58. Distribution of ^{14}C in extracts of irradiated aqueous solutions of [1-*phenyl*-^{14}C]fenamiphos (Dime *et al.*, 1983, revised 1985).

Component	^{14}C, % of applied, after (hours)						
	0	1	2	4	6	12	24
Organosoluble							
F	94.3	78.7	64.1	43.7	28.1	9.6	4.3
FSO	4.0	2.7	7.0	8.4	11.2	16.0	17.3
Rf > Fenamiphos	--	2.2	2.7	2.0	2.4	1.1	1.3
Rf < Fenamiphos	--	1.9	2.8	3.7	5.5	2.9	2.8
Diffuse	1.4	3.6	6.0	10.9	11.4	10.9	5.3
Origin	<0.1	0.4	1.2	2.2	3.1	4.1	3.3

Component	^{14}C, % of applied, after (hours)						
	0	1	2	4	6	12	24
Subtotal	99.7	89.5	83.8	70.9	61.7	44.6	34.3
Water-soluble							
Band 7 (Rf = 0.95)		0.1	0.1	0.2	0.4	0.4	0.1
Band 6 (Rf = 0.91)		0.1	0.2	0.2	0.3	0.5	0.4
Band 5 – FSOP		0.3	0.6	1.1	1.3	1.1	1.1
Band 4 (Rf = 0.54)		0.2	0.5	0.7	1.0	1.0	1.1
Band 3 – FSA		0.7	1.4	2.1	3.1	4.4	6.1
Band 2 – FPSA		2.3	5.6	10.5	14.3	17.1	18.6
Band 1 (Rf = 0.10)		0.4	0.7	1.5	1.9	2.3	3.3
Origin [2]		1.4	3.2	6.0	9.1	14.4	20.8
Diffuse [1]		0.6	1.2	2.6	3.4	4.8	4.9
Subtotal	0.3	6.1	13.5	24.9	34.8	46.0	56.4
Total recovered ^{14}C	100	95.6	97.3	95.8	96.5	90.6	90.7

FSA fenamiphos sulfonic acid FPSA fenamiphos phenol sulfonic acid

The rapid degradation of fenamiphos was confirmed in another irradiation study (Andersen, 1985a). Solutions of fenamiphos were irradiated with a TQ 150 high-pressure mercury vapour lamp fitted with a Duran 50 filter tube to pass wavelengths >290 nm in a rotary carousel irradiation apparatus. Analysis by HPLC indicated a half-life of 15 minutes. Photoproducts were not identified. The UV spectrum of fenamiphos (3.8 mg/l in distilled water) over the range 200-249 nm showed a maximum at 284 nm. The conclusion of the study was that the UV absorption properties of the compound indicate that fenamiphos would undergo photodegradation under environmental conditions.

Environmental fate in water/sediment systems

The degradation of [1-*phenyl*-^{13,14}C]fenamiphos was investigated in a laboratory study (Wilmes, 1987) in two water/sediment systems obtained from a reclaimed gravel pit (Lienden) and an orchard drainage ditch (Ijzendoorn) in The Netherlands. Both systems were treated with 10 mg of labelled fenamiphos/l applied to the sludge, and samples were analysed 1, 7, 26, 54 and 98 days after application. Water and sludge were separated and the water samples analysed by reversed-phase HPLC with a radioactivity detector. The sediment samples were extracted with MeOH and with MeOH/H_2O (1:1) containing 0.2% H_3PO_4. Measurement of ^{14}C in the extracts by liquid scintillation counting was followed by HPLC. The remaining solids were compressed and analysed by combustion and LSC. Volatiles were collected in traps.

In both systems, the distribution of the radioactivity between the water and sediment remained constant for the duration of the study. The results are shown in Table 59. In the Lienden samples, the radioactivity in the water ranged from 76 to 86% and in the Ijzendoorn samples from 51 to 62% of the applied radioactivity. The rate of degradation was faster in the Lienden samples, with almost complete transformation from fenamiphos to fenamiphos sulfoxide and fenamiphos sulfoxide phenol by day 98. The major identified product was fenamiphos sulfoxide.

Table 59. Distribution of ^{14}C from fenamiphos in water/sediment systems (Wilmes, 1987).

Phase, site, DAT	Distribution of radioactive residues as % of recovered radioactivity (mean of duplicates)					
	F	FSO	FSOP	FSO_2P	Unidentified	Total % found
Water						
Lienden						
1	81.1	2.5				83.6
7	69.1	12.2				81.3
26	66.1	9.8				75.9
54	7.2	69.3	5.1	1.7[1]	2.6	85.9

Phase, site, DAT	Distribution of radioactive residues as % of recovered radioactivity (mean of duplicates)					
	F	FSO	FSOP	FSO_2P	Unidentified	Total % found
98	–	66.7	10.9	4.6	3.4[1]	85.6
Ijzendoorn						
1	56.8	2.1				58.9
7	54.7	7.5				62.2
26	51.9	2.7				54.6
54	35.1	15.6	2.5		2.6	55.8
98	31.1	15.7	1.0	1.8	1.6	51.2
Sediment						
Lienden						
1	14.0	0.1[1]			1.5	15.6
7	15.3	0.5[1]			2.2	18.0
26	19.3	0.4			1.6	21.3
54	3.3	3.1	0.4 (total FSOP + FSO_2P)		2.4	9.2
98	0.8	3.2	0.3 (total FSOP + FSO_2P)		6.3	10.6
Ijzendoorn						
1	35.1	0.4			3.8	39.3
7	31.7	0.9	0.7 (total FSOP + FSO_2P)		2.5	35.8
26	37.3	2.8			2.8	42.9
54	30.6	2.3			2.3	33.2
98	29.3	2.4			2.4	34.1

[1]Single analyses

In an addendum to the above study the degradation of [1-*phenyl*-$^{13/14}$C]fenamiphos was investigated at two concentrations in the Lienden system after a 29-day period (Wilmes, 1988). The results after 29 and 26 days are compared in Table 60.

Table 60. Comparison of degradation of fenamiphos in water/sediment system from Lienden after 26 and 29 days (Wilmes, 1987, 1988).

Sample	^{14}C, % of applied		
	29 days, 10 mg/l	29 days, 1 mg/l	26 days*, 10 mg/l
Water phase			
F	47.4	21.2	66.1
FSO	43.8	58.6	9.8
Sediment extract			
F	8.6	7.5	19.3
FSO	2.3	4.6	0.4
Total F	55.9	28.7	85.4
Total FSO	46.1	63.2	10.2

* Original experiment

At day 29, 44% of the radioactivity in the water was due to fenamiphos sulfoxide compared to 10% at day 26 in the original study. There was also increased degradation of fenamiphos at the lower concentration.

Proposed degradation pathways of fenamiphos in aquatic systems are shown in Figure 4. In summary, fenamiphos is degraded by the familiar mechanisms of oxidation of the methylthio group, cleavage of the phosphate ester bond and further degradation to CO_2. An additional pathway involves the formation of fenamiphos phenol sulfonic acid by oxidative demethylation of the methylthio group before cleavage of the ester.

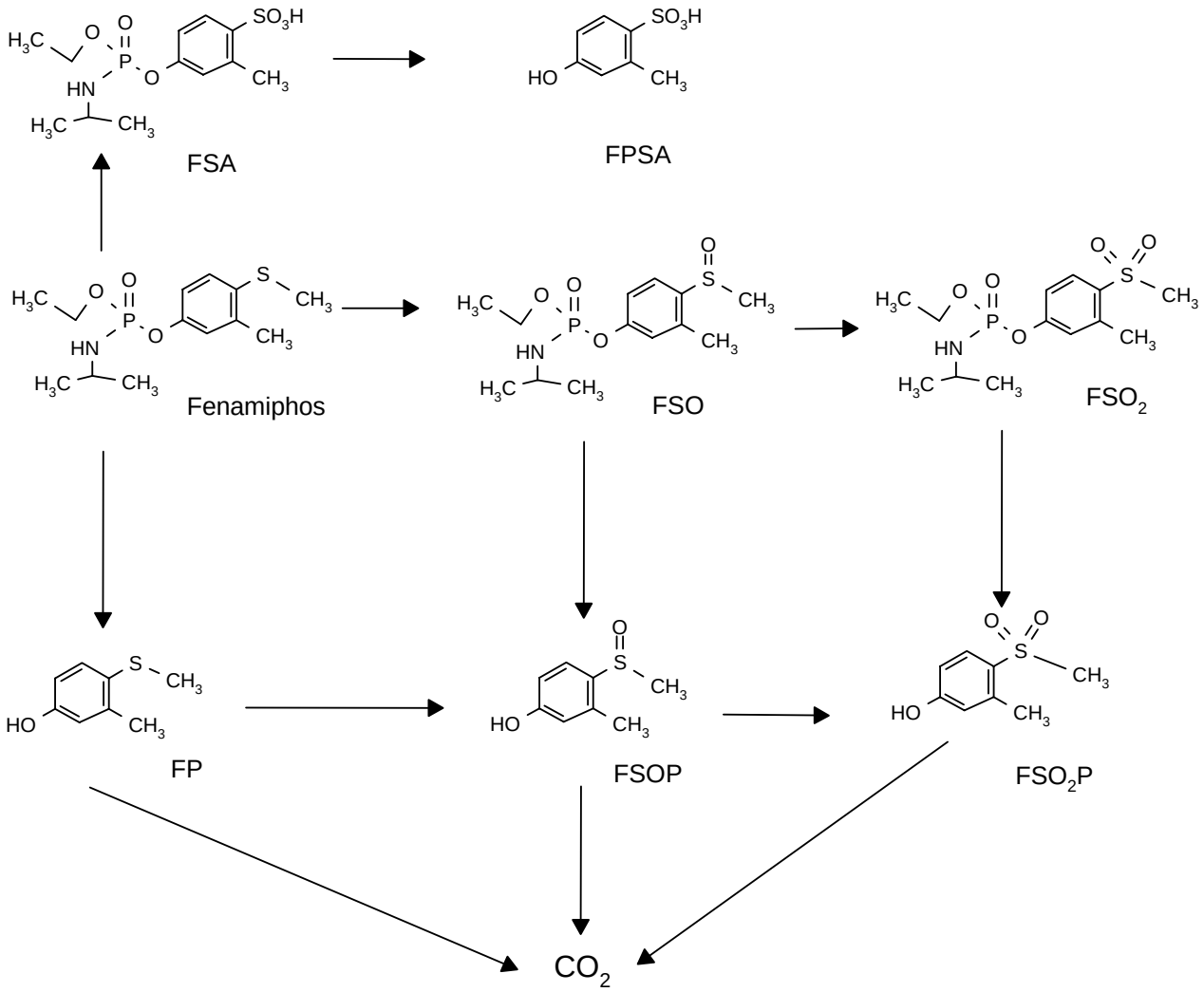
METHODS OF RESIDUE ANALYSIS

Methods for the determination of fenamiphos and its sulfoxide and sulfone in various crops, animal tissues, water and soil were reported by the manufacturer. In addition, multi-residue enforcement methods were submitted by the governments of The Netherlands and Australia.

Enforcement methods

In the Official Methods of Analysis in The Netherlands, fenamiphos residues are determined by GLC with an ion-trap detector. The limit of determination for fenamiphos is reported as 0.05 mg/kg for various types of sample, and recoveries from lettuce were 55-70%, with fortifications at 0.07-0.35 mg/kg. In fatty foods the limit of determination was also reported as 0.05 mg/kg; recoveries were not

Figure 4. Proposed degradation pathways of fenamiphos in the aquatic environment.



FSO	fenamiphos sulfoxide	FSO_2	fenamiphos sulfone
FP	fenamiphos phenol	FSOP	fenamiphos sulfoxide phenol
FSO_2P	fenamiphos sulfone phenol	FSA	fenamiphos sulfonic acid
FPSA	fenamiphos phenol sulfonic acid		

reported. The LOD in the multi-residue method appears to be for fenamiphos alone and not total fenamiphos residues.

In a multi-residue method provided by the Australian government fenamiphos is determined by GLC with flame photometric detection in the phosphorus mode. The limit of determination is reported as 0.02 mg/kg.

The published method devised by Thornton (1971) was included as an enforcement method by the manufacturer. It is described in detail below.

Published methods for enforcement also include the general methods for the determination of organophosphorus pesticides of Hild and Thier (1979) and Specht and Thier (1987).

Other general methods

A general method for the determination of organophosphorus pesticide residues in non-fatty foods was reported by Storherr *et al.* (1971). This method was used in Brazil for the determination of fenamiphos in tomatoes, bananas, cotton and coffee.

Samples containing less than 5% sugar are blended with CH_3CN and Celite, then filtered by vacuum. Samples containing about 5-15% sugar (e.g. fruits) are blended with CH_3CN and water and filtered. An aliquot of the filtrate is extracted three times with CH_3Cl. The CH_3Cl extracts are combined and drained through a Celite-charcoal column. The column is eluted with CH_3CN/C_6H_6 (1:1) and the eluate concentrated to about 1.0 ml by evaporation. Isopropanol is added and the mixture distilled to remove the CH_3CN. This procedure is repeated once. Finally, the residue is concentrated to about 0.5 ml and made up to 1.0 ml with ethyl acetate.

About 3-8 µl are injected onto a 300 x 2.2 mm i.d. glass column, 2% stabilized diethylene glycol succinate on 80-100 mesh Chromosorb W (IIP) (column temperature, 200-220°C). Organophosphorus pesticides are detected by their retention times with a thermionic alkali detector (TID). At fortification levels of 0.05-0.2 mg/kg, recoveries from various crops were in the range 72-122%.

Forty-one organophosphorus pesticides were evaluated, but they did not include fenamiphos or its metabolites.

Specialized methods

Methods for the determination of fenamiphos and its metabolites in numerous crops, animal tissues, water and soil were reported. All are modified versions of the method of Thornton (1969, 1971). The original method was validated for citrus peel and pulp, pineapple fruit, peanut kernels and hulls, cured tobacco, peanut vines, pineapple bran and pineapple forage. The basic procedure involves homogenisation of the sample with dry ice and acetone, filtration to remove solids, and extraction of the filter cake with CH_3Cl. The CH_3Cl extract is added to the filtrate and the phases are separated. The CH_3Cl phase is dried and concentrated to near dryness. The remaining residue is extracted twice with CH_3Cl and washed with 0.05 *N* H_2SO_4. The CH_3Cl extracts are combined and evaporated to dryness. The residue is dissolved in acetone and treated with 0.1 molar $KMnO_4$ and 20% $MgSO_4$. The mixture is extracted with CH_3Cl and the extracts dried and evaporated. The remaining residue is dissolved in a measured volume of acetone and quantified by GLC as fenamiphos sulfone. With oily substrates such as oilseeds and fats, the oxidized residues are cleaned up on a Florisil column before evaporation and quantification.

Peanut kernels and animal tissues are chopped, blended with acetone and filtered. The filter cake is extracted twice with CH_3Cl, and the extracts are combined and partitioned. The CH_3Cl phase is filtered through Celite and evaporated to dryness. The residue is dissolved in petroleum ether and partitioned against CH_3CN. The lower CH_3CN phase is separated and washed with petroleum ether, which is itself washed with CH_3CN. The combined CH_3CN phases are evaporated to dryness in a rotary evaporator at 40°C.

After oxidation, the samples and the standard are dissolved in acetone and an appropriate aliquot is injected into the gas chromatograph (30 cm x 4 mm borosilicate glass column, 6% QF-1 solution coated on 80-100 mesh Gas Chrom Q, helium as carrier gas at 100 ml/min, phosphorous-sensitive alkali-flame detector).

Recoveries of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone from numerous crops are shown in Table 61. All analyses were with the original Thornton method (1969, Report 25402), or one of the variants listed by Report number. Where no Report number is given, the original method was used.

Table 61. Recoveries from crop samples by method 00024/I8 or a modification.

Sample	Fortification level, mg/kg	% recovery			Report no.
		F	FSO	FSO_2	
Orange peel	0.02	95,105	100, 100	95, 100	91361
	0.05	90	108	102	
dry peel	0.05	69			45952
	0.1	89	125	110	
pulp	0.02	85, 90	85, 90	75, 85	91361
	0.05	108	86	96	
	0.1		79	94	
leaves	0.5	71	114	131	45952
molasses	0.1	121			
oil	1	70			45952
wash water	0.05	127			45952
Peanut kernels	0.1	96	96	79	
hulls	0.1	71		89	
vines	0.5	84	97		
Pineapple pulp	0.05	76, 84	74, 104	74, 88	80476, 82388
	0.1	95, 100	91	94	
bran	0.05	80, 84	74, 86	74, 84	80476, 82388
	0.1	87, 91		108	
forage	0.1	76	79	82	
foliage	0.05	88	86	88	80476
crown	0.05	86, 92	76, 88	78, 84	80476, 82388
	0.1	101			
Apples	0.1	96, 86, 98, 97, 76	95	75	80664, 43979
	0.05	82, 95	90, 76	80, 79	
Cherries	0.01			130	80432
	0.02			105	80432
	0.03			103	80432
	0.05	77, 84, 98	82, 86, 112	78, 88, 92, 102	43979, 80432
	0.1	83, 92, 92	73, 77, 81	82, 87, 90, 103	43979
Peaches	0.05	78, 97	96, 97	66, 78	80704, 43979
	0.1	82	80	72	
Broccoli	0.05	110	80	73	43979
	0.05	94		94	35778
Cauliflower	0.05	86, 80	88	80, 88	43979, 35778
	0.1	100			35778
Brussels sprouts	0.01	50,50	70, 70	60, 70	87381,
	0.02	50	65	85	
	0.05		98	78, 92, 96	
	0.05	84		70	35778
	0.1	95			
Cabbage	0.05	114		86	35778
Carrot	0.05	94		90	35778
	0.1	93		68	35778
Sugar beet tops	0.05	90, 106		92, 118	35778
root	0.05	100, 102, 116		78, 104, 116	35778
juice	0.1	88, 94		110	
	0.05	98			
pulp	0.1	76		105	

Sample	Fortification level, mg/kg	% recovery			Report no.
		F	FSO	FSO_2	
Sweet potatoes	0.05 0.1	78 81, 90		76	35778
Coffee beans	0.05 0.1 0.5	86 79, 86 77	70	78	84626
Cotton seed	0.05	135	118	84	66584
Grapes	0.01 0.02 0.03 0.05 0.1	80 80 97 102, 108, 110 98, 101	 92, 92 100	 94, 108 102	 66584, 69911, 68204 68204, 69399
Raisins Raisin trash	0.05 0.05	80 67	53 124	84 57	69459
Grapefruit	0.1	87, 96, 97, 121	93, 94, 120, 121	99,93	69913
Lemons pulp peel	0.02 0.05 0.02 0.05	90, 100 82 65, 90 80	75, 90 72 80, 90 102	70, 95 92 85, 85 84	91360 91360

Modifications to the published method of Thornton (1971) for specific crops are described below.

Ohs (1988a) reported a modification (M002) for the determination of fenamiphos and its sulfoxide and sulfone in tomatoes. Samples are homogenized and blended with acetone. The homogenate is filtered and the filter cake is blended again with acetone. The combined filtrates are concentrated by rotary evaporation (60°C), leaving an aqueous phase which is cleaned up on an Extrelut 20 cartridge. The parent compound and metabolites are eluted with CH_2Cl_2 and the eluate is concentrated to dryness. The residue is taken up in acetone and a 20% $MgSO_4$ and 0.2 M $KMnO_4$ solution is added. After 20 minutes, the reaction mixture is cleaned up on Extrelut 20 as described above. The evaporated residue is taken up in ethyl acetate. GLC is on a Megabore column (SE 54 L, 30 m, 0.53 mm i.d.) at a temperature of 200°C (injector temperature 270°C) with an FPD. Recoveries were 91% at 0.02 mg/kg and 100% at 0.20 mg/kg. The typical limit of determination is given as 0.02 mg/kg.

Specht (1995) reported a modification to M002 for bananas (Supplement E019). Fenamiphos sulfone is determined by gas chromatography on a DB-5 30 m fused silica capillary column, 0.53 mm i.d., with a thermionic alkali FID. Temperatures: column 150°C to 250°C; injector 250°C; detector 270°C. Retention time for fenamiphos sulfone: 18 min. Recoveries of fenamiphos sulfone at 0.02, 0.045 and 0.45 mg/kg ranged from 64 to 97%.

Ohs (1998b) reported in Supplement E020 recoveries from bananas at fortification levels of 0.02 and 0.1 mg/kg fenamiphos of 86-88% and 82-91% respectively, with a limit of determination of 0.02 mg/kg, and in Supplement E022 recoveries from watermelons at 0.02 and 0.1 mg/kg of 93 and 87% respectively. The limit of determination was again 0.02 mg/kg.

Recoveries from carrots at fortification levels of 0.02 and 0.1 mg/kg were 88 and 91% (Ohs, 1989, Supplement E024). The limit of determination was 0.02 mg/kg.

Method 0024/I8 and modification M002 were revised for the extraction of tobacco, banana pulp and peel, strawberries, melons, peppers, tomatoes and summer squash (zucchini) by Blass (1997a,b). After clean-up of the raw extract on an Extrelut cartridge as in M002, the evaporated residue is transferred to a silica gel cartridge with diethyl ether. Fenamiphos and its sulfoxide and sulfone are eluted with methanol. The oxidation procedure follows.

At fortification levels of 0.02 to 5.0 mg/kg the recoveries were 74 to 101%. The limit of determination is 0.02 mg/kg for carrots and 0.1 mg/kg for tobacco (green and dried). It should be noted that the oxidation may be affected by small volumes of water co-eluted from the Extrelut cartridge. It is recommended that the eluate from the cartridge is dried with anhydrous sodium sulfate and filtered. Recoveries at fortification levels of 0.02, 0.10 and 1.0 mg/kg ranged between 72 and 110% for banana pulp and peel, strawberries, melons, peppers, tomatoes and summer squash.

Other modifications to method 0024/I8 include the following.

Brussels sprouts, Report 87381. Celite 545 was substituted for Hyflo Super-Cel; Whatmann 1 was substituted for Whatmann 42 filter paper.

Cherries, Report 80432. After oxidation a heptane/acetonitrile clean-up was incorporated, with 20 ml heptane + 20 ml acetonitrile followed by a second extraction of the heptane phase with 10 ml of acetonitrile.

Lemon pulp, Report 91360. The sample (25 g) is extracted with 150 ml acetonitrile/water (3:2). The extrelut cartridge of M002 is eluted with chloroform instead of dichloromethane. After oxidation the residue is taken up in acetonitrile and partitioned against hexane.

Orange pulp, Report 91361. Orange pulp (25 g) is extracted twice with 150 ml of acetone. CH_2Cl_2 replaces CH_3Cl in the extraction and oxidation steps.

Many of the modifications were to the gas-chromatographic conditions. The modifications (including proposed confirmatory columns) are shown in Table 62, together with conditions reported in the original method.

Table 62. Gas-chromatographic conditions for method 00024/I8 and its modifications.

Report No., Sample	Column dimensions	Column packing	Carrier gas (ml/min)	Temperatures, ° C, column injector detector
25402 Method 00024/I8	30.5 cm x 4 mm i.d. borosilicate glass	6% QF-1, 80/100 mesh, Gas Chrom Q	Helium (100)	230 225 240
Modifications:				
80664 Apples	20 cm x 4 mm i.d.	6% QF-1, 80/100 mesh Chromosorb W,HP	Nitrogen (80)	205 260 245
87381 Brussel sprouts	61 cm x 2 mm i.d. glass	5% OV-17, 80/100 mesh Gas Chrom Q	Nitrogen	203 230 240
80432 Cherries	38 cm x 2 mm i.d. glas	Ultrabond II (Supelco)		210 280 250
84626 Coffee	80 cm x 4 mm i.d.	10% DC-200, 80/100 Chromosorb CW, HP	Nitrogen (100)	215 255 210
69399 Grapes	40 cm x 2 mm i.d.	10% DC-200 + 1.5% OV-210 80/100 mesh Chromosorb W, HP		
69459 Dried raisins	61 cm x 6 mm o.d.	3% OV-210, 80/100 mesh Gas Chrom Q	Nitrogen (110)	240 250 200
69911 Grapes	20.3 cm x 6.3 mm o.d.	3% OV-210, 80/100 mesh Gas Chrom Q	Nitrogen (100)	225 230 200
69913 Grapefruit	40.6 cm x 2 mm i.d. glass	15% OV-210, 80/100 mesh	Helium (40)	200 280

Report No., Sample	Column dimensions	Column packing	Carrier gas (ml/min)	Temperatures, ° C, column injector detector
		Chromosorb W, HP		250
91361 Orange pulp	61 cm x 2 mm i.d.	15% OV-12 x 1.95% OV-210		
80704 Peaches	45.7 cm x 6.3 mm o.d.	3% OV-225 100/120 Gas Chrom Q	Nitrogen (135)	235 230 200
	91.4 cm x 6.3 mm o.d.	3% OV-1 100/120 Chrom W, HP	Nitrogen (150)	240 200 230
	91.4 cm x 6.3 mm o.d.	3% OV-1 100/120 Chrom W, HP	Nitrogen (150)	240 220 230
	45.7 cm x 6.3 mm o.d.	3% OV-210 100/120 Chrom W, HP	Nitrogen (130)	235
80476 Pineapple	91.4 cm x 6.3 mm o.d.	3% OV-1 100/120 mesh Chrom W, HP	Nitrogen (150)	245
82388 Pineapple	20 cm x 4 mm i.d.	6% QF-1 80/100 mesh Chromosorb W, HP	Nitrogen (90)	195 255 220

Method 00224/I389 for the determination of des-isopropyl fenamiphos sulfoxide (DIFSO) and fenamiphos and its sulfoxide and sulfone in crops was reported by Sandie and Gronberg (1981). DIFSO has been detected as a minor and transient metabolite in grapes and citrus. The method has been used in processing studies on grapes, pineapples, peanuts and cotton seed.

Chopped fruit samples are blended with acetone and diluted with water. The extract is filtered and divided into two equal portions, both of which are partitioned three times with CH_3Cl. The CH_3Cl phases are combined and evaporated. The residues are taken up in ethyl acetate and partitioned against water. The ethyl acetate phase is discarded and the water phase partitioned against CH_3Cl. The CH_3Cl is evaporated and the residue dissolved in 20% CH_3CN/H_2O. Portion A (containing F, FSO and FSO_2) is oxidized as previously described and partitioned with CH_3Cl. Portion B is chromatographed in small volumes by HPLC on RP-18 in 20% CH_3CN/H_2O solvent (with UV detection at 220 nm) and the DIFSO fractions are collected and combined. CH_3CN is added before evaporation to dryness. The remaining residue is derivatized by dissolution in BF_3/methanol and allowed to stand overnight at room temperature. Water is added and the DIFSO is extracted with CH_3Cl.

For GLC the fraction containing F, FSO and FSO_2 is dissolved in ethyl acetate and injected onto a borosilicate column (40 cm x 2 mm i.d.; 10% C-200 + 1.5% OV-210 on 80/100 mesh Chromosorb W). The residue is quantified as the sulfone. The DIFSO residue is dissolved in ethyl acetate and injected onto a 25 cm x 2 mm i.d. borosilicate column packed with 5% OV-225 on 60/80 mesh Tenax. The methylated DIFSO is identified by its retention time.

Recoveries of DIFSO from orange peel and pulp at 0.05 mg/kg were 93-102% and from grapes at 0.1 mg/kg or above 83-84%. At levels of 0.01 to 0.05 mg/kg, recoveries ranged from 34 to 115%. The limit of determination was 0.01 mg/kg. Recoveries of F, FSO and FSO_2 from orange peel and pulp fortified at 0.1 mg/kg were 90–118%. The limit of determination was 0.01 mg/kg.

Animal tissues

The determination of fenamiphos and the metabolites FSO, FSO_2, FSOP, FSO_2P, DIF, DIFSO and $DIFSO_2$ in cattle tissues and milk was reported by Sandie *et al.,* (1978, Method I 270).

Chopped tissue samples except fat are homogenized with acetone and Super-Cel (Celite). The extract is filtered, the filter cake is again extracted with CH_2Cl_2 and acetone, and the extracts are combined. After phase separation, the lower phase is drained through Na_2SO_4 into a flask and evaporated. The residue is taken up in hexane and partitioned twice with acetonitrile. The combined CH_3CN layers are divided into two equal portions and both are evaporated to dryness.

Chopped fat samples are homogenized with hexane and Super-Cel and filtered. The filter cake is suspended in CH_3CN and again filtered. The filtrates are combined and the same procedure as for other tissues is then followed.

Milk is blended with acetone and Super-Cel. The extract is filtered and the filter cake is suspended in CH_2Cl_2 and acetone. The filtrates are combined and shaken, and after phase separation the lower phase is filtered through Na_2SO_4 and concentrated by rotary evaporation. The remaining aqueous layer is once more extracted with dichloromethane and acetone. After phase separation the lower phase is added to the previous one and the combined extract is evaporated to dryness. The residue is dissolved in hexane and partitioned twice with acetonitrile. The combined CH_3CN extracts are divided into two equal portions and evaporated to dryness as before.

One portion of the dry residue is oxidized with $KMnO_4$ (0.1 molar) in $MgSO_4$ (20% solution) and extracted with CH_2Cl_2. The CH_2Cl_2 extract is dried over Na_2SO_4 and evaporated to dryness. The residue is partitioned between hexane and CH_3CN and the CH_3CN phase is washed with hexane. The combined acetonitrile phases are evaporated to dryness. The residue is dissolved in ethyl acetate and 5-µl aliquots are injected into a gas chromatograph equipped with a borosilicate glass column and flame photometric detector (FPD) in the phosphorus mode. Fenamiphos sulfone is identified by its retention time.

The residue from the other half of the sample is dissolved in ethyl acetate and hydrolysed for 10 min in a mixture of benzene and 0.5 N KOH in isopropyl alcohol. The reaction mixture is then transferred to a separatory funnel with isopropyl alcohol and water. After the addition of benzene and shaking, the phases are allowed to separate. The lower aqueous phase is drained into a second separatory funnel and the benzene phase is again partitioned against water. The combined aqueous phases are acidified by the addition of 3 N HCl and partitioned with CH_2Cl_2. The lower phase is drained through Na_2SO_4 and the partitioning is repeated twice.

After adding 100 µl of 10% mineral oil in hexane, the combined CH_2Cl_2 fractions are evaporated to dryness on an analytical evaporator. The residue is then methylated by adding 0.5 ml of 0.2 M trimethylanilinium hydroxide in methanol and analysed by GLC with an FPD in the sulfur mode.

Recoveries from fortified tissues were 87-117% at 0.1 mg/kg and 73-158% at 0.05 mg/kg in the phosphorus mode, and 84-138% at 0.1 mg/kg and 58-148% at 0.05 mg/kg in the sulfur mode. The limit of determination for all tissues in both modes was 0.01 mg/kg.

Recoveries from fortified milk were 79-115% at 0.005 mg/kg in the phosphorus mode and 84-128% at 0.01 mg/kg and 70-120% at 0.005 mg/kg in the sulfur mode. The limit of determination in both modes was 0.001 mg/kg.

A method for the determination of F, FSO and FSO_2 in soil and turf was reported by Peterson and Winterlin (1986). Samples are homogenized and extracted with ethyl acetate/acetone (4:1). The extract is filtered and the filter cake again extracted. The filtrates are combined and filtered through anhydrous Na_2SO_4. After evaporation to near dryness the residue, dissolved in benzene, is adsorbed onto a Florisil column. The column is washed with 2.5% acetone in benzene, and fenamiphos and FSO_2 are eluted with 25% acetone in benzene. Fenamiphos sulfoxide is eluted with 80% acetone in benzene. Fenamiphos and its sulfone are further chromatographed on a cellulose column with 25% acetone in benzene. The fraction containing fenamiphos and FSO_2 and that containing FSO are

separately evaporated to dryness and redissolved in appropriate volumes of ethyl acetate and acetone respectively. The samples are analysed by capillary GLC with an NPD (capillary: DB-5, 25 m x 0.251 mm i.d. at 235°C, hydrogen as carrier gas).

Recoveries of fenamiphos averaged 90.2% from soils fortified at 0.005-1.0 mg/kg wet soil and those of fenamiphos sulfoxide and fenamiphos sulfone averaged 83.3% and 95.4% respectively. In turf grass, recoveries of all three compounds were similar. The limit of determination in soil was 0.005 mg/kg and in turf grass 0.01 mg/kg.

The determination of fenamiphos and its sulfoxide and sulfone in water at a limit of 0.1 µg/l was reported by Vorkink (1989). A 500-ml sample is extracted three times with aliquots of CH_3Cl. The combined extracts are evaporated to a volume of 3-5 ml, then transferred to an N-EVAP tube evaporator with gas flow and taken to dryness under nitrogen. The residue is redissolved in toluene and analysed by GLC on a capillary column (25% cyanopropyl, 3 m x 0.2 mm i.d. fused silica) with an NPD.

The recoveries of fenamiphos, FSO and FSO_2 from spiked water were 86.5%, 95.9% and 78.3% respectively at 0.1 µg/l and 101%, 101%, and 102% at 0.5 µg/l. The limit of determination was 0.1 µg/l for all three compounds, with linearity in the range 0.1 to 10 µg/l.

An HPLC method for the determination of fenamiphos phenol sulfoxide, phenol sulfone and phenol sulfonic acid in soil to support terrestrial field dissipation studies was reported by Mattern and Parker (1994). Soil (50 g) is extracted with methanol/water (2:1) and filtered. The filter cake is extracted once more with methanol/water and the filtrates are combined. Methanol is removed by rotary evaporation and the remaining aqueous filtrate is partitioned three times with ethyl acetate. The aqueous phase and the combined ethyl acetate phases are cleaned up separately.

The aqueous phase is passed through an amino-SPE cartridge which is eluted with 0.01 M NH_4OH. The eluate is neutralized with 0.1 M acetic acid, evaporated to dryness at <40°C, and the residue dissolved in water. The organic fraction is evaporated to dryness, redissolved in ethyl acetate, concentrated to <0.1 ml under a stream of nitrogen, diluted in isopropanol/ethyl acetate (3:1) and passed through a 1-g silica gel SPE column which is eluted with the isopropanol/ethyl acetate solvent. The eluate is evaporated under nitrogen and the residue is dissolved in methanol/water (1:1).

The solution from the aqueous fraction is chromatographed by ion-pairing with 0.005 M tetrabutylammonium hydroxide (TBAH) on a reverse-phase C-18 column at pH 5 with a gradient of increasing acetonitrile. The cleaned-up organic fraction is chromatographed on a similar column with 0.1% acetic acid and an increasing proportion of acetonitrile. Detection of all compounds is by UV absorption at 240 nm.

Recoveries of fenamiphos phenol sulfoxide were 88.2 to 111.9% with an average of 97.4%, of fenamiphos phenol sulfone 101.6 to 107.0% with an average of 104.6%, and of fenamiphos phenol sulfonic acid 76.0 to 99.9% with an average of 86.0%. The limits of determination in soil were 0.01 mg/kg for the three analytes.

A method combining electrospray LC-MS-MS and conventional HPLC (Mattern *et al*., 1998) was also developed to determine fenamiphos and five degradation products in soil in support of field dissipation studies. An internal deuterated fenamiphos standard (0.1 ml of 25 mg/l in acetonitrile) is added to the soil sample (25 g), followed by CH_3CN/water (4:1). The mixture is sonicated for 1 min and filtered, and this extraction is repeated. The CH_3CN is removed by evaporation and the aqueous solution diluted to 50 ml with 1% methanol in water. An aliqot of 1-2 ml of this solution is filtered through a 0.45 µm acrodisc into an autosampler vial for LC-MS-MS analysis. A 100-µl aliquot of this is injected onto an HPLC column (Phenomenex Prodigy 5 ODS-2, 50 x 3.2 mm, 5 µm) and chromatographed with a gradient system from 5 mM NH_4OAc/10% methanol with an increasing

proportion of methanol. The mass spectrometer is operated in the positive-ion mode and optimized to monitor the daughter ions of each analyte.

The remaining aqueous phase from the original acetonitrile/water extract (45 ml) is passed through a 2-g C-18 cartridge conditioned with methanol followed by water. The aqueous eluate is collected and the cartridge rinsed with 7 ml water which is added to the eluate. The cartridge is then eluted with CH_3CN. The organic eluate is evaporated on a Turbovap evaporator and the residue dissolved in 0.5 ml of acetonitrile and diluted to 2.5 ml with water. An aliquot of this is filtered through an acrodisc and transferred into an autosampler vial for the HPLC determination of fenamiphos and its sulfoxide and sulfone. The aqueous eluate from the C-18 cartridge is evaporated to dryness on a rotary evaporator, the residue is dissolved in 2.5 ml of water, and an aliquot is filtered through an acrodisc into an autosampler vial for HPLC determination of the phenol sulfonic acid.

A 200-µl aliquot is injected into a switched 2-column HPLC (column 1 Alltech Econosil C-18 cartridge; 250 x 4.6 mm i.d., 10 µm; column 2 MetaChem Inertsil ODS-2, 250 x 4.6 mm i.d., 5 µm; column-switching system) and chromatographed with a gradient system of 0.1% H_3PO_4 and increasing proportions of acetonitrile. Detection is by UV absorption at 240 nm. The recoveries of the six analytes are shown in Table 63.

Table 63. Average recoveries of fenamiphos and 5 degradation products from soil.

Analyte	Fortified at 0.01 mg/kg	Fortified at 0.1 mg/kg
Fenamiphos	106	102
Fenamiphos sulfoxide	104	104
Fenamiphos sulfone	106	106
Fenamiphos phenol sulfoxide	92	95
Fenamiphos phenol sulfone	87	95
Fenamiphos phenol sulfonic acid	77	84

The limit of determination of each analyte in the test soil was 0.01 mg/kg.

Stability of pesticide residues in stored analytical samples

Lenz (1995) fortified 12 crop commodities with a mixed standard containing fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone at 1.0 mg/kg of each component. The samples were held in frozen storage (≤-5° C) and analysed after 1, 3, 6, 12, and 18 months. The method used measured all the residues as fenamiphos sulfone by GLC with a thermionic alkali detector.

There was <10% loss or decomposition of fenamiphos residues in garlic and wet and dry grape pomace after 12 months, and in asparagus, bananas, grapes, grape juice, cotton seed, cotton seed meal, and refined cotton seed oil after 18 months. There was <20% decomposition in raisins and cotton seed hulls after 18 months. The results are shown in Table 64.

Freeseman and Zoloty (1995) conducted a storage stability study of fenamiphos in cow tissues for 89 days and in milk for 61 days.

Fat was extracted with hexane, and kidney, liver, and muscle were individually extracted with acetone, and the extracts fortified at 1 mg/kg with fenamiphos (F), des-isopropyl fenamiphos (DIF), fenamiphos sulfoxide (FSO), des-isopropyl sulfoxide (DIFSO), sulfone (FSO_2), or des-isopropyl sulfone ($DIFSO_2$). The fortified extracts were stored at –25°C for 3 months, then analysed by HPLC. Cow milk was fortified at 1 mg/kg with F, FSO, or FSO_2 and stored at -25° C for 2 months before analysis.

Fenamiphos and its metabolites were relatively stable (<20% degradation) in kidney and muscle extracts. In the liver extracts only DIFSO and $DIFSO_2$ showed extensive degradation, 52% and 45% respectively. In the fat extracts only fenamiphos, DIF, and $DIFSO_2$ showed >50% degradation. The fenamiphos residues were stable in milk (<5% degradation).

Table 64. Stability of fenamiphos residues (sum of fenamiphos, fenamiphos sulfoxide and sulfone) in fortified plant material at -5°C (Lenz, 1995).

Commodity	Storage period, days	% recovery
Asparagus	43	94
	92	93
	180	89
	364	93
	553	92
Banana	92	86
	180	94
	364	100
	553	98
Cotton seed	43	51
	96	91
	180	100
	380	100
	538	100
Cotton seed hulls	43	98
	98	75
	180	90
	384	96
	538	81
Cotton seed meal	40	68
	93	92
	177	73
	377	84
	535	96
Cotton seed oil, refined	40	96
	95	98
	177	100
	377	100
	535	100
Garlic	34	96
	102	98
	208	99
	368	96
Grapes	34	93
	92	73
	184	84
	366	99
	547	99
Grape juice	34	99
	92	97
	184	92
	366	83
	547	100
Wet grape pomace	41	96
	155	99
	418	100
Dry grape pomace	41	99
	155	97
	418	81
Raisins	36	74
	95	82
	175	99
	359	92
	548	84

Under the conditions used to store the samples in the dairy cattle feeding study described later (Wargo, 1978), fenamiphos, if present, could have been degraded to FSO, but all FSO and FSO_2 residues would have remained relatively stable.

In the first part of the analytical method described above for the determination of fenamiphos and its metabolites in animal tissues and milk (Sandie *et al.,* 1978), both fenamiphos and FSO are oxidized to FSO_2, which is quantified as part of the total fenamiphos residue. Any degradation of fenamiphos and FSO to FSO_2 in the original extracts would not affect the total level of FSO_2 determined.

In the second part of the method, the total fenamiphos residues are determined by converting the oxidized fenamiphos, des-isopropyl-fenamiphos and DIFSO to sulfone phenols and determining the methylated phenols. Since DIF and DIFSO are both oxidized to $DIFSO_2$ before hydrolysis and methylation the observed degradation of DIF to DIFSO would not affect the total amount of methylated phenols.

DIFSO and $DIFSO_2$ are degraded to the corresponding phenols, but neither DIFSO nor $DIFSO_2$ was detected in the liver or kidney in the most recent goat metabolism study (Weber and Ecker, 1993), and $DIFSO_2$ was present in flank muscle but not detected in loin or round muscle. DIFSO and $DIFSO_2$ would therefore not be expected to be present at significant concentrations in the tissues of cattle, and their instability would not have a marked effect on the overall results of the analyses.

In an earlier storage stability study (Lenz, 1977), ^{14}C ring-labelled DIF, DIFSO and $DIFSO_2$ were added to tissues and milk at 1 mg/kg and stored at –10°C. DIFSO and $DIFSO_2$ were unstable in the liver, kidney and fat, where degradation was predominantly to the corresponding phenols, but were relatively stable in the milk and muscle. The findings are in agreement with the Freeseman and Zoloty study and are recorded in Table 65.

Table 65. Stability of fenamiphos residues in milk and animal tissues stored at –10°C.

Sample	Storage, days	% recovery of					
		F	FSO	FSO_2	DIF	DIFSO	$DIFSO_2$
Milk	0	96	100	99			
	1				100	95	100
	23						
	38				100	74	87
	61	96	100	100			
	78				74	63	88
Fat	0	95	100	100	96	98	97
	1				100	95	85
	21				94	74	45
	30				81	85	46
	83	42					
	88				3		
	89		92	99		85	47
Kidney	0	95	100	99	80	99	100
	3				98	89	81
	7				93	94	71
	51				81	80	48
	83	79					
	88				88		
	89		100	99		96	91
Liver	0	90	100	99	80	97	95
	1				100	91	82
	7				96	60	46
	14				100	57	45
	83	75					
	84				81	80	48
	88				88		
	89		98	99		40	49

Sample	Storage, days	% recovery of					
		F	FSO	FSO_2	DIF	DIFSO	$DIFSO_2$
Muscle	0	94	100	99	95	99	100
	1				100	92	90
	83	79					
	88				86, 87	82	83
	89		100	99		97	92

F	fenamiphos	DIF	Desisopropyl-fenamiphos
FSO	fenamiphos sulfoxide	DIFSO	Desisopropyl-fenamiphos sulfoxide
FSO_2	fenamiphos sulfone	$DIFSO_2$	Desisopropyl-fenamiphos sulfone

Definition of the residue

The existing definition of the residue is “sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos”. The analytical methods allow all three compounds to be included in the determined residue because fenamiphos and the sulfoxide are both oxidized to the sulfone, so the existing residue definition is appropriate on the basis of the metabolism studies reviewed.

USE PATTERN

Fenamiphos is an organophosphorus nematicide which is registered for use in more than sixty countries. It provides effective control of free-living, root-knot and cyst-forming nematodes. The main target species are *Meloidogyne spp., Pratylenchus spp., Radopholus similis, Rotylenchus spp., Rotylenchus reniformis, Heterodera spp.* and *Xiphenma spp.* Fenamiphos provides crop protection against nematode damage through systemic activity in the plant and also contact action in the soil.

Fenamiphos is marketed as “Nemacur” and formulated into a granular product (5, 10, 12 and 15 GR) or an emulsion concentrate at 400 g ai/l. In the USA the EC product is formulated at 360 g ai/l.

Fenamiphos may be applied pre-planting, at planting, in established crops or in seedbeds and nurseries. For effective control, it is important that the Nemacur formulations are incorporated into the soil in the zones of root growth, as these are exposed to nematodes. Fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone all exhibit nematicidal activity, thereby providing prolonged activity.

Fenamiphos is predominantly used in tropical and sub-tropical areas in the USA, South America, South Africa, Spain, Australia, Costa Rica and Italy. The product is mainly applied to bananas, citrus fruit, grapes, peanuts, tobacco and vegetables.

Information on numerous registered use patterns was provided by the manufacturer. GAP was also reported by the Australian government. Registered uses are shown in Table 66.

Table 66. Registered uses of fenamiphos.

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
Apple	Chile	400 EC	Seedling stage	Pre-planting root immersion or spray	40 g ai/100 l	1		19
			Post-planting	 In furrow irrigation Drip irrigation	0.4-0.6 g ai/plant 6-8 2.8-4.8	1	45	
	Dominican Republic	12 GR		Incorporation	0.8-1.2 (2.4-4.8 g ai/plant)		60	
	Honduras	12 GR		Incorporation	0.8-1.2 (2.4-4.8 g ai/plant)		60	
	Mexico	10 GR 400 EC		Spreading Spray	2 g ai/m height of tree 6 g ai/tree		45-72	

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
	Spain	10 GR 400 EC		Spreading/incorp. Spraying	5-10	1	90	
	USA	350 EC		Incorporation	5.45-8.2		72	47
Asparagus	Colombia	10 GR	At planting Established crop	Spreading/incorp.	0.1 g ai/plant 2.5 (0.2 g ai/plant)			
	Mexico	10 GR	After the final cutting	Spreading/drilling	1.2-1.5	2		
Avocado	Dominican Republic	12 GR		Incorporation	0.8-1.2 (2.4-4.8 g ai/plant)		60	
	Honduras	12 GR		Incorporation	0.8-1.2 (2.4-4.8 g ai/plant)		60	
Banana	Argentina	10 GR		Spreading	12 g ai/plant		60	1
	Australia	100 G		Spreading/incorp.	2.5 g ai/plant 1.8 g ai/plant	3		2 1,3
		400 liq.		Soil treatment	24 9.6-12	3		2,6 3,7
	Brazil	10 GR		Spreading/incorp.	2-3 g ai/plant	2	30	
	Colombia	10 GR	At planting At 3 months	Incorporation	1.5 g ai/plant 3 g ai/plant	1-3	60	 20
	Costa Rica	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Ecuador	10 GR 15 GR		Spreading	3 g ai/plant	3		25
	El Salvador	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Greece	10 GR 400 EC	At planting Subsequent applications	Incorporation	2 g ai/plant 3-4 g ai/plant 2-4 g ai/plant	1-3	28-42	 27
	Guatemala	10 GR 15 GR 400 EC		Spreading/incorp.	5 5.1 2.8-6.8	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Mexico	10 GR 400 EC	At planting 4 to 6 months after first application	Spreading Spreading Spraying	1.5-2.5 g ai/corm 3 g ai/irrigation channel 16-32 g ai/10 l	1 2-3	60	
	Nicaragua	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Portugal	10 GR 400 EC	Growing fruit	Spreading Spraying	10 2-4 g ai/plant	1		
	South Africa	10 GR	At planting	Incorporation	30-50 g/mat	2		
	Spain	10 GR 400 EC		Spreading/incorp.	1.5-3 g ai/plant 10-20		60 90	
Beans	Argentina	10 GR		Spreading	3.2-4	1	90	1
	Italy	5 GR		Soil incorporation	10-15	1	20	
	Spain	10 GR 400 EC	Pre-planting	Spreading Spraying	5-10 8-10	1	90	
Beetroot	Australia	400 liq.	7 days before planting	Soil treatment	9.6 9	1	84	
Brassicas	Costa Rica	10 GR	At planting Established crops	Spreading/incorp. Band treatment	1 g ai/hole 2-3			
Brussels sprouts	Mexico	10 GR 400 EC		In drills Spraying	1.5-3 3-5 (total/season) 1.6-3.2			
	USA	15 GR	Before planting	Incorporation	6.7 (31-78 g ai/304.8 m 6.7 [1000 ft] row)	1		
Cabbage	Costa Rica	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Guatemala	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	4-6	1	60	

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
	Mexico	10 GR 400 EC		In drills Spraying	1.5-3 3-5 (total/season) 1.6-3.2			
	Nicaragua	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	USA	15 GR	Before planting	Incorporation	6.7 (31-78 g ai/304.8 m [1000 ft] row)			
Carrots	Australia	100 G	7 days before seeding	Incorporation Band treatment	9	1	84	
		400 liq.	7 days before planting	Soil treatment	9.6	1	84	9
	Costa Rica	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Guatemala	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Italy	5 GR	At planting	Soil incorporation	15	1	90	
	NZ	400 EC	At sowing	Incorporation	3			
	Nicaragua	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
Celery	Australia	400 liq.	7 days before planting	Soil treatment	9.6	1	84	9
Cherry	Chile	400 EC	Seedling stage	Pre-planting root immersion or spray	40 g ai/100 l	1		19
			Post-planting	 In furrow irrigation Drip irrigation	0.4 0.6 g ai/plant 6-8 2.8-4.8	1	45	
	USA	350 EC		Incorporation	5.45-8.2		45	47
Citrus	Australia	400 liq.	Spring		30 15	1 1		 8
	Dominican Republic	12 GR		Incorporation	0.8– 1.2 (2.4-4.8 g ai/plant)		60	
	Greece	10 GR 400 EC		Spreading	3-4 g ai/m^2		28-42	
	Honduras	12 GR		Incorporation	0.8– 1.2 (2.4-4.8 g ai/plant)		60	
	South Africa	10 GR 400 EC		Spreading Spraying	12 (40 g ai/tree) 12		150	
	USA	350 EC		Incorporation	1.63-8.2	1-2	30	50
Cocoa	Brazil	10 GR	At transplanting	Soil treatment	0.05 g ai/plant		45	
	Mexico	10 GR 400 EC	Nursery plants Transplanting	Incorporation Spraying	1-3 g ai/m^2 6-8 g ai/tree 2-2.4 g ai/m^2 60-80 g ai/shrub		45	
Coffee	Brazil	10 GR		Incorporation	1-1.5 g ai/plant 7 g ai/plant	3	45	16 17
	Colombia	10 GR	At planting 1st year	Spreading/incorp.	1-1.5 g ai/plant 2.5-4 (1-2 g ai/plant)	1-2 2	60	 21
	Costa Rica	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Dominican Republic	10 GR 12 GR 15 GR		Spreading/incorp.	5 2.4-3.6 5.1	1	60	
	El Salvador	12 GR 12.6 GR		Spreading/incorp.	2.4-3.6 3.5-5	1	60	 26
	Guatemala	10 GR 12 GR 12.6 GR 15 GR 400 EC		Spreading/incorp.	5 2.4-3.6 3.5-5 5.1 5.6-6.8; 2.8-3.4	1	60	 26 33
	Honduras	10 GR 12 GR 12.6 GR		Spreading/incorp.	5 2.4-3.6 3.52-5	1	60	 26

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
		15 GR			5.1			
	Mexico	10 GR	Nursery plants Transplanting	Incorporation	0.2 g ai/bag 1-1.5 g ai/plant	1	45	
	Nicaragua	10 GR 12.6 GR 15 GR		Spreading/incorp.	5 3.52-5 5.1	1	60	26
	Panama	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
Cotton	Brazil	10 GR	At planting	Incorporation	3-5	1	98? nil	
	Greece	10 GR 400 EC	At sowing	Incorporation	1-2 8; 2-3.4		28-42 60	29
	Mexico	10 GR 400 EC	At planting	In drill Spraying	1.5-2 1.5-2			
	South Africa	10 GR	At planting	In furrow	15 g ai/100 m row			
	Spain	10 GR 400 EC	Pre-planting	Spreading/incorp.	5-10 4.8-10	1	90	
	USA	150 GR 350 EC		In furrow Band spray	0.84-1.65 0.82-3.27	1		45
Crucifers	Australia	100 G	7 days before transplanting	Incorporation into soil	9-11	1		
		400 liq.	Pre-planting; 7 days before planting	Soil treatment	9.6	1		
Cucumber	Argentina	10 GR		Spreading	3.2-4	1	90	1
	Colombia	10 GR		Spreading	0.5-0.8 g ai/plant		60-90	
	Costa Rica	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Guatemala	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Nicaragua	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Spain	10 GR 400 EC	Pre-planting	Spreading/incorp.	5-10 8-10	1	90	
Cucurbits	Australia	400 liq.	7 days before planting	Soil treatment	9.6	1		9
Egg plant	Italy	5 GR		Soil incorporation	10-15	1	20	
	USA	15 GR 350 EC	At transplanting	Band treatment Incorporation	2.25 2.18	1		
Garlic	Colombia	10 GR	At sowing and 60 days later	Spreading	0.5 g ai/m^2 0.5 g ai/plant	2	60	
	Mexico	10 GR 400 EC	At planting	In drill Incorporation/Spray	1.5-3 2.4-3.2			
	USA	15 GR	At planting	In furrow	2.5-5	1		
Ginger	Australia	100 G	Mid Nov, late Jan	Spreading	11	1		
	South Africa	10 GR	At planting	In furrow	100 g ai/100m row	1	250	
Grapes	Argentina	10 GR	At sprouting	Spreading	3.2-4	1	60	1
	Australia	400 liq.	Late Sept.	Soil treatment to inter–vine row	12			10
	Chile	400 EC	Seedling stage	Pre-planting root immersion or spray	40 g ai/100 l	1		19
			Post-planting	 In furrow irrigation Drip irrigation	0.4-0.6 g ai/plant 6-8 2.8-4.8	1	45	
	Colombia	10 GR	At planting	Spreading	0.5 g ai/plant	1	45	
			Young plants		1-2 g ai/plant		45	
			In production		2-3 g ai/plant		45	
	Ecuador	10 GR 15 GR		Spreading	5-10	1		
	Mexico	10 GR 400 EC	At nursery At planting At sprouting Pest activity	Spreading Band application	1-1.5 g/m^2 4-6 4-6 0.4-0.6		Nil 20	

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
	South Africa	10 GR 400 EC	Before bud burst or after harvest	Spreading/incorp.	1 g ai/m^2 or 100 g ai/100 m row	1	100	
	Spain	10 GR 400 EC		Spreading Spraying	5-10 8-10	1	90	
	USA	350 EC		Incorporation	1.63-6.54		2	48
Grapefruit	Argentina	10 GR		Spreading	3.2-4	1	60	1
	Costa Rica	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Guatemala	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Mexico	10 GR 400 EC		Spreading Spray	1-2 g ai/m height of tree 8 g ai/l water		180	
	Nicaragua	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
Guava	South Africa	10 GR	In spring	Spreading	3 g ai/m^2		120	38
Kiwifruit	NZ	400 EC	At planting	Soaking	16 g ai/10 l soln.			
	USA (CA)	350 EC		Soil treatment	1.63-3.27		31	49
Lemons	Chile	400 EC	Seedling stage	Pre-planting root immersion or spray	40 g ai/100 l	1		19
			Post-planting	 In furrow irrigation Drip irrigation	0.4-0.6 g ai/plant 6-8 2.8-4.8	1	45	
	Colombia	10 GR		Spreading	20 g ai/plant		180	
	Costa Rica	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Guatemala	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Mexico	10 GR 400 EC		Spreading Spray	1-2 g ai/m height of tree 8 g ai/l of water		180	
	Nicaragua	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
Lettuce (endive)	Australia	400 liq.	7 days before planting	Soil treatment	9.6	1	56	9
Litchi	South Africa	10 GR	In spring	Spreading	3 g ai/m^2	1	70	38
Lucerne	NZ	400 EC		Spot treatment	8.8-10			
Mandarins	Colombia	10 GR		Spreading	10-20 g ai/plant		180	
Mangoes	Dominican Republic	12 GR		Incorporation	0.8-1.2 (2.4-4.8 g ai/plant)		60	
	Honduras	12 GR		Incorporation	0.8-1.2 (2.4-4.8 g ai/plant)		60	
Melons/ watermelon	Argentina	10 GR		Spreading	3.2-4	1	90	1
	Brazil	400 EC	At sowing	Trickle irrigation	4	1		
	Colombia	10 GR		Spreading	0.5-0.8 g ai/plant		90	
	Costa Rica	10 GR 15 GR		Spreading/incorp.	2.5-5 2.5-5.1	1	60	
	Dominican Republic	10 GR 12 GR 15 GR		Spreading/incorp.	2.5-5 0.72-1.2 2.5-5.1	1	60	
	El Salvador	10 GR 12 GR 15 GR		Spreading/incorp.	2.5-5 0.72-1.2 2.5-5.1	1	60	

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
	Guatemala	10 GR 12 GR 15 GR		Spreading/incorp.	2.5-5 0.72-1.2 2.5-5.1	1	60	
	Honduras	10 GR 12 GR 15 GR		Spreading/incorp.	2.5-5 0.72-1.2 2.5-5.1	1	60	
	Italy	5 GR		Incorporation	10-15	1	20	
	Nicaragua	10 GR 15 GR		Spreading/incorp.	2.5-5 2.5-5.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	2.5-5 2.5-5.1	1	60	
	Spain	10 GR 400 EC	Pre-planting	Spreading Spraying	5-10 8-10	1	90	
Mushrooms	Australia	400 liq.		Spray to compost at turning	22-26 g ai/tonne compost	1	42	11
				Casing treatment	22 g ai/tonne of casing	1	42	12
Nectarines	South Africa	400 EC	At establishment	Spraying	1 g ai/m^2		100	42
	USA	350 EC		Incorporation	5.45-8.2		45	47
Olives	Colombia	10 GR		Spreading	20-30 g ai/plant			
Okra	Mexico	10 GR 400 EC		In drill Spray	1.2-1.5 1.2-1.6			
	USA	15 GR	At planting	Incorporation	2.25-2.8	1		
Onions	Argentina	10 GR		Spreading	3.2-4	1	90	1
	Australia	400 liq.	7 days before planting	Soil treatment	9.6	1	84	9
	Colombia	10 GR	At sowing and 60 days later	Spreading	0.5 g ai/m^2 0.5 g ai/plant	2	60	
	Italy	5 GR		Soil incorporation	10-15	1	20	
	South Africa	400 EC	At planting	Incorporation	3	1	80	
Oranges	Argentina	10 GR		Spreading	3.2-4	1	60	1
	Chile	400 EC	Seedling stage	Pre-planting root immersion or spray	40 g ai/100 l	1		19
			Post-planting	 In furrow irrigation Drip irrigation	0.4 0.6 g ai/plant 6-8 2.8-4.8	1	45	
	Colombia	10 GR		Spreading	10-20 g ai/plant		180	
	Costa Rica	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Guatemala	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Honduras	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Italy	5 GR		Soil incorporation	10-15	1	180	
	Mexico	10 GR 400 EC		Spreading Spray	1-2 g ai/m height of tree 8 g ai/l water		180	
	Nicaragua	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	5 5.1	1	60	
	Spain	10 GR 400 EC		Spreading Spraying	5-10 8-10	1	90	
Papaya	South Africa	10 GR	Early spring	Incorporation	4 g ai/m^2			
Parsnips	Australia	100 G (100 g/kg)	7 days before seeding	Incorporation Band treatment	9	1	84	
		400 liq.	7 days before planting	Soil treatment	9.6	1	84	9
Peaches	Italy	5 GR		Soil incorporation	10-15	1	120	
	Mexico	10 GR 400 EC		Spreading Spray	2 g ai/m height of tree 6 g ai/tree		45-72	
	South Africa	400 EC	6 weeks after establishment	Spraying/incorporation	1 g ai/m^2		100	42
	USA	350 EC		Incorporation	5.45-8.2		45	47

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
Peanuts	Costa Rica	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Dominican Republic	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	El Salvador	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Guatemala	10 GR 15 GR 400 EC		Spreading/incorp.	4-6 2.8-3.4; 5.6-6.8	1	60	 33
	Honduras	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Mexico	10 GR 400 EC	At planting	Incorporation	1.5-3 1.6-3			
	Nicaragua	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	4-6	1	60	
	South Africa	10 GR 400 EC	At planting After planting	In furrow Spraying	15 g ai/100m row 1.6-3.2	1	63	39
	USA	15 GR 400 EC	At planting	Incorporation Spray in row	1.68-2.85 1.63-2.70	1		44
Peas	South Africa	400 EC	Pre-planting	Incorporation	1.6		90	41
Pecan nuts	South Africa	10 GR	In spring	Spreading	1 g ai/m^2	1	120	
Peppers	Argentina	10 GR		Spreading	3.2-4	1	90	1
	Dominican Republic	12 GR		Spreading/incorp.	0.72-1.2	1	60	
	Guatemala	12 GR		Spreading/incorp.	0.72-1.2	1	60	
	Honduras	12 GR		Spreading/incorp.	0.72-1.2	1	60	
	Spain	10 GR 400 EC	Pre-planting	Spreading Spraying	5-10 8-10	1	90	
Pineapples	Australia	100 G	Bed preparation	Soil incorporation	100 g ai/100m of bed	1		4
		400 liq.	Pre-plant bed treatment	Soil treatment	100 g ai/100m of bed	1		4
			Plant and ratoon crop	Foliar spray	2.4	5		13
			Ratoon crop	Foliar spray	4.8	2		14
	Colombia	10 GR	At planting Established crop	Spreading	0.1 0.2 g ai/plant 1-1.5 g ai/plant	1-2	60	 22
	Costa Rica	10 GR 15 GR		Spreading/incorp.	7-14 7.5-14.1	1	60	
	Dominican Republic	10 GR 12 GR 15 GR		Spreading/incorp.	7-14 2.4-3.6 7.5-14.1	1	60	
	El Salvador	10 GR 12 GR 15 GR		Spreading/incorp.	7-14 2.4-3.6 7.5-14.1	1	60	
	Guatemala	10 GR 12 GR 15 GR 400 EC		Spreading/incorp.	7-14 2.4-3.6 7.5-14.1 2.8-6.8	1 1-2	60 60	
	Honduras	10 GR 12 GR 15 GR		Spreading/incorp.	7-14 2.4-3.6 7.5-14.1	1	60	
	Mexico	10 GR 400 EC	At planting At planting	Spreading/incorp. Spray	4-6 10 4		30	 34
	Nicaragua	10 GR 15 GR		Spreading/incorp.	7-14 7.5-14.1	1	60	
	Panama	10 GR 15 GR		Spreading/incorp.	7-14 7.5-14.1	1	60	
	South Africa	400 EC	At root formation	Spraying	2.5	3	56	40
	USA* USA**	15 GR 350 EC	Pre-planting Pre-planting Post planting	Incorporation Foliar spray Spraying	10 5.4-9.8 9.8 0.54-3.27		 225 30	46 52 51
Potato	Argentina	10 GR	At planting	Spreading	2	1	90	1
	Australia	100 G	Pre-planting	Soil incorporation	10	1	84	
		400 liq.	Pre-planting and emergence	Soil treatment	5.2	1	84	
	Brazil	10 GR	At planting	Spreading/incorp.	4	1	100	
	Chile	400 EC	To planted or sown crop	Spraying	4-10	1	45	
	Colombia	10 GR	At planting and after	Spreading	2-3	2	45-60	

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
			germination					
	Costa Rica	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Dominican Republic	12 GR		Incorporation	0.72-1.2	1	60	
	Greece	10 GR 400 EC	At planting	Spreading/incorp.	6-8 4		28-42 60	 28
	Guatemala	10 GR 12 GR 15 GR			2.5-5 0.72-1.2 2.55-5.1			
	Honduras	10 GR 12 GR 15 GR			2.5-5 0.72-1.2 2.55-5.1	1	60	
	Italy	5 GR		Soil incorporation	10-15	1	20	
	Mexico	10 GR 400 EC	At planting	In drill Incorporation	4-6			
	NZ	400 EC	At planting	Broadcast spray	8			
	Nicaragua	10 GR 15 GR			2.5-5 2.55-5.1	1	60	
	Panama	10 GR 15 GR			2.5-5 2.55-5.1	1	60	
	Portugal	10 GR	21 days before planting	Spreading	8-10			
	South Africa	400 EC	At planting	Spraying in furrow Aerial	10 1.6 1.2	1 6	42	 43
	Spain	10 GR 400 EC	Pre-planting (20 days before sowing)	Spreading Spraying	10 8-10	1	120	
Raspberry	USA	350 EC		Incorporation	3.27-6.54	1	90	
Soya bean	Mexico	10 GR 400 EC		In drill Spray	1.2-2		270	
Strawberry	Australia	100 G	Within one month of planting	Spreading	0.1 g ai/plant	1	42	5
		400 liq.	7 days before planting	Soil treatment	9.6	1	42	15
	Italy	5 GR		Soil incorporation	10-15	1	20	
	USA	15 GR 350 EC	Before transplanting	Incorporation	2-3 1.96-2.94	1	110	
Sugar beet	Greece	10 GR 400 EC	At sowing	Soil treatment	3 8	1	28-42 60	 30
	Italy	5 GR		Soil incorporation	10-15	1	20	
	Spain	10 GR 400 EC	Pre-planting	Spreading Spraying	5-10 10-20	1	90	
Sugar cane	Australia	100 G	From planting to early tillering	Band treatment	4	–		
		400 liq.	From planting to early tillering	Directed treatment	4			
Sweet potato	Australia	400 liq.	7 days before planting	Soil treatment	9.6	1	84	9
	NZ (kumara)	400 EC	At planting	Broadcast/incorporation	8			
Tomato	Argentina	10 GR		Spreading	3.2-4	1	90	1
	Australia	100 G	7 days before planting	Spreading; band treatment	11	1		
		400 liq.	7 days before planting	Soil treatment	9.6	1		15
	Brazil	10 GR	At planting	Incorporation	3-4	1	90	18
	Chile	400 EC	To planted or sown crop	Spraying	4-10	1	45	
	Colombia	10 GR	Before of after sowing At transplanting	Spreading/incorp.	1.5-2.5 g ai/m^2 0.2-0.4 g ai/plant	1 2	60-90	23
	Costa Rica	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Dominican Republic	10 GR 12 GR 15 GR		Incorporation	2.5-5 0.72-1.2 2.55-5.1	1	60	
	Ecuador	10 GR 15 GR		Spreading	1.3-3 1.5-3			
	El Salvador	10 GR 15 GR		Spreading/incorp.	2.5-5 2.55-5.1	1	60	
	Guatemala	10 GR 12 GR 15 GR		Incorporation	2.5-5 0.72-1.2 2.55 –5.1	1	60	
	Honduras	10 GR		Incorporation	2.5-5	1	60	

Crop	Country	Form.	Application				PHI, days	Notes
			Timing	Method	Rate, kg ai/ha	No.		
		12 GR 15 GR			0.72-1.2 2.55 –5.1			
	Italy	5 GR		Soil incorporation	10-15	1	20	
	Nicaragua	10 GR 15 GR		Incorporation	2.5-5 2.55 –5.1	1	60	
	Panama	10 GR 15 GR		Incorporation	2.5-5 2.55 –5.1	1	60	
	Portugal	10 GR 400 EC		Spreading Spraying	3.4; 3 35 3.2 36	1 1	90 90	
	South Africa	10 GR 400 EC	Pre-planting	Incorporation	1 g ai/m 100 g ai/100 m row	1		
	Spain	10 GR 400 EC	Pre-planting	Spreading Spraying	5-10 8-10	1	90	
Vegetables ***	Greece	10 GR 400 EC	Before planting	Incorporation Spraying	6-8; 4 31 4-8; 6 8; 4 32		28-42 60	

*Puerto Rico only.
** Hawaii only.
***Vegetables include tomato, eggplant, peppers, melon, watermelon, cabbage and cauliflower.

1. Can be applied by machinery connected to the tractor or in a steady trickle in the sowing furrow.
2. For previously untreated ratoons, where re-treatment is late or where nematode populations are high.
3. Treatment of plant crops and subsequent ratoon crops.
4. 100 g ai/100 m of bed for a 1 m wide band; *e.g.* for 0.75 m bed apply 75 g ai/100 m of row.
5. 100 g ai/1000 plants or 0.1 g ai/plant.
6. 2.4 g ai/stool or 240 g ai/100 m of row or 2.4 g ai/m^2 of wetted area.
7. 120 g ai/100 m of row or 1.2 g ai/stool or 1.2 g ai/m^2 of wetted area.
8. Initial rate is 30 kg ai/ha or 3 g ai/m^2 for trickle irrigation and maintenance rate is 15 kg ai/ha or 1.5 g ai/m^2 for trickle irrigation.
9. 9.6 kg ai/ha or 6.4 g ai/10 m of row.
10. 12 kg ai/ha or 1.2 g ai/m^2 for trickle irrigation.
11. Apply treatment to compost before peak heating at the last turn of compost (20 L of spray mixture/tonne of compost), or after peak heating to compost.
12. 4 g ai/bale of peat weighing 50 to 60 kg or 22 g ai/tonne of casing. Do not treat both casing and compost.
13. Plant crop and ratoon crop foliar spray. Apply 5 sprays at 2 to 3 month intervals beginning 1 month after planting and ending no later than 6 weeks after flower induction. Immediately after plant crop harvest, apply 2 sprays over the plants 2 to 3 months apart.
14. Ratoon crop foliar spray only. If nematodes have infested roots during the plant cycle, apply after harvest of plant crop and an additional spray 4 to 6 weeks later.
15. 9.6 kg ai/ha or 6.4 g ai/10 m of row (trickle irrigation included).
16. When planting incorporate 1.5 g ai/plant into the hole. On 2 year old coffee plants apply 1 g ai/plant in October, January and April. On coffee plants 3 years old or over, apply 1.5 g ai/plant in October, January and April.
17. Label not dated.
18. On staked tomatoes apply 0.2 g ai/plant before transplanting the seedlings; the product should be scattered into the hole then incorporated in the soil.
19. Root immersion at 40 g ai/100 l. Immerse for 30 minutes or spray for seedlings in bags.
20. When in production, apply 3 g ai/plant every 4-5 months at the beginning of the rainy season.
21. In the first year apply twice at 1-2 g ai/plant or 2.5-4 kg ai/ha; in subsequent years apply at the same rate twice a year.
22. For established plants apply 1-1.5 g ai/plant every 5 to 6 months.
23. 1.5-2.5 g ai/m^2, equivalent to 1.25 to 2.5 kg ai/ha.
24. 1-1.5 g ai/m^2 of seedbed.
25. Apply every 4 months.
26. For plants less than 1 year old apply 0.6 g ai/plant and for plants older than 1 year apply 1 g ai/plant. Apply once a year in May, June or beginning of July.
27. For existing infections apply at 4 g ai/plant then following applications every 3-4 months at 3 g ai/plant.
28. Spraying in sowing row or with drip irrigation.
29. Before sowing apply 8 kg ai/ha; for existing crops apply 2 to 3.4 kg ai/ha with a drip irrigation system.
30. Apply 8 kg ai/ha as a soil treatment before sowing; apply 3 kg ai/ha with a drip irrigation system in existing plantations.
31. Apply 6 to 8 kg ai/ha to the soil and incorporate; apply 4 kg ai/ha in the sowing or plantation row; apply 0.8 g ai/ha in the planting hole.
32. Apply 4 to 8 kg ai/ha in the row at transplantation or 6 to 8 kg ai/ha as a soil spray before planting or apply 4 kg ai/ha as a spray to the planting row or for drip irrigation.
33. Apply 5.6 to 6.8 kg ai/ha as a broadcast spray or 2.3 to 3.4 kg ai/ha as a band treatment.
34. Apply to foliage in established plantations at 90 and 150 days.
35. Apply 3.4 kg ai/ha 7 to 14 days before planting; apply 3 kg ai/ha 30 days after planting.
36. For drip irrigation only; first application before planting; second application 30 days after planting.

37. Commence application at planting or in established plantations in August. In all cases one application should be made in August followed by another in January; applications should be repeated annually in August and January.
38. Apply follow-up treatment annually in spring at 1.5 g ai/m^2
39. 63 days for harvest and for use of peanut fodder.
40. Use on the plant crop only. Apply at the first signs of root formation; 2 subsequent sprays are applied at 3 month intervals. A total of 3 crop sprays per crop cycle are required.
41. Do not harvest peas within 90 days of application; do not allow animals to graze pea hay within 120 days of application.
42. Apply within 6 weeks of establishment of young trees in spring and in March-April (after harvest). Apply in 1m^2 around each tree. Repeat the 2 sprays during the second year, thereafter a treatment after harvest may be made annually.
43. Western Cape only: apply a total of 6 sprays at 1.6 kg ai/ha; first 3 sprays should be applied at weekly intervals commencing at 7 to 10 days after emergence of the plants. The 4th and subsequent sprays are applied at 14-day intervals. For aerial application (1.2 kg ai/ha) a total of 7 sprays are required. Commence spraying 7 to 10 days after plant emergence and repeat at 7-day intervals.
44. Do not feed or graze green peanut vines or peanut hay. Do not hog down treated peanut fields.
45. Do not feed or graze cotton foliage.
46. Post-plant applications can be made in addition to the pre-plant application. Do not apply more than a total of 20 kg ai/ha per crop per season, regardless of the formulation or method of application. Do not use forage or fodder for animal feed.
47. Do not apply more than 8.2 kg ai/ha per year per planting site. Do not graze livestock in treated orchards. Do not feed cover crops grown in treated orchards to livestock.
48. Apply a maximum of 6.54 kg ai/ha per season as a band treatment or low pressure irrigation. The last application may be made up to 2 days before harvest. Do not graze or feed treated crop to livestock.
49. Apply a maximum of 6.54 kg ai/ha per year. Do not graze livestock in treated vineyards. Do not feed cover crops grown in treated vineyards to livestock.
50. For band treatment two applications may be made per season not exceeding 8.2 kg ai/ha. For low pressure irrigation do not exceed a maximum of 6.7 kg ai/ha per season (1.63 to 3.27 kg ai/ha). Do not graze livestock in treated areas. In Florida apply a maximum of 5.45 kg ai/ha for band treatment and for low pressure irrigation apply a maximum of 4.9 kg ai/ha per season.
51. Post-plant application: do not apply more than a total of 26.2 kg ai/ha per plant crop including a pre-plant application. Post-plant applications may be made to the plant crop at 1 to 3 month intervals by foliar spray or drip irrigation. Do not apply more than a total of 9.8 kg ai/ha to each ratoon crop. The first application to the ratoon may be made immediately after crop harvest. Do not use green forage or green fodder for animal feed (cannery waste, such as cull fruit, fruit skin or shells, crowns, cores and basal ends may be fed).
52. Puerto Rico only: apply specified dosage as a foliar spray; begin applications 1 to 3 months after planting. First ratoon crop: make the first application immediately after crop harvest. Do not apply more than a total of 20 kg ai/ha per crop per season regardless of the formulation or method of application. Do not use forage or fodder for animal feed.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data were provided on supervised trials on numerous crops including carrots, onions, Brussels sprouts, cabbage, peppers, squash, tomatoes, melons, grapefruit, lemons, limes, oranges, apples, cherries, peaches, grapes, bananas, pineapple, peanuts, cotton and coffee. For each crop, the relevant GAP is tabulated with the residue data for ease of comparison.

Residue data, application rates and spray concentrations have been rounded to 2 significant figures, or for residues near the limit of detection to 1 significant figure. Although the trials included control plots, no control data are reported unless residues in the untreated samples exceeded the limit of determination. Results of trials according to GAP are underlined; results used to estimate STMRs are double underlined. All residues, unless otherwise stated, are defined as “sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos”. The limit of determination in each trial is indicated at the end of each Table or in the text if reference is made to validation of a specific method.

Carrots. Trials were conducted in Australia, Italy and Spain. Field reports were not provided for any of the trials in Australia or Spain, nor for some in Italy, so the results are tabulated without any further details (Table 67). Recoveries from carrots using standard method 00024/I8 are reported in Table 61 (Report no. 35778) at fortification levels of 0.05 and 0.1 mg/kg; recoveries from other trials are reported in the footnotes to Table 67.

In trials in Italy (Heinemann and Ohs, 1997a) Nemacur 10 GR was applied at 15 kg ai/ha to soil before sowing carrots. The granules and carrot seed were scattered manually and incorporated with a rotary cultivator at depths of 5 cm (trials 501581 & 506664) and 10 cm (trials 506672 &

506680). Trial plots were 100 m^2 and the soils were sand, clay, and sandy loam. The treatments were applied 90 or 91 days before harvest of the first carrots; samples of roots were prepared by lightly washing in cold water. Details are shown in Table 67.

In subsequent trials (Heinemann and Ohs, 1997b) Nemacur 10 GR was applied to the soil at 30 kg ai/ha, twice the rate in the first trials, before sowing carrots. The granules and carrot seed were scattered manually and incorporated with a rotary cultivator at depths of 5 cm (trials 602752 & 603562) and 10 cm (trials 603570 & 603589). Trial plots were 40 to 80 m^2 and the soil at three sites was sandy; no information was given for the fourth site. The treatments were applied 90 days before the first carrots were harvested. The samples were cleaned with paper before extraction.

Two further trials were conducted at two sites in Italy in 1996 (Ohs, 1998). Nemacur 5 GR or 10 GR was applied to seedbeds before sowing carrots at a rate of 15 kg ai/ha. The plot sizes were 98 m^2 and the soils were sandy (pH 7.9 and 0.2% C). The products were spread by hand and incorporated with a rotary hoe. Samples were taken at 90, 100, 131 and 143 days after application; adhering soil was removed by rinsing with cold water.

Table 67. Residues from supervised trials on carrots in Australia, Spain and Italy.

Location, year (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Australia, (VIC), 1972	400 EC	8.96	1*	107 117 136	'baby' carrot	0.05 0.04 0.02	Bayer Australia 1971a 27/71a [1]
Australia, (VIC), 1971	400 EC	8.96	1**	93 103 122	'baby' carrot	0.08 0.07 0.04	27/71b [1]
Australia, (VIC), 1971	400 EC	13.44	1**	93 103 122	'baby' carrot	0.13 0.1 0.09	27/71c [1]
Australia, (VIC), 1986 (Western red)	10 GR	11	1	84	root (early maturity)	0.02	Bayer Australia 1986 18/86a [2]
Australia, (VIC), 1986 (Western red)	10 GR	22	1	84	root (early maturity)	0.05	18/86b [2]
Spain, (Cadiz), 1981 (Tim tom)	10 GR	10	1	136	root	0.05, 0.06	Bayer 1981a 5200-81 [3]
Spain, (Cadiz), 1981 (Tim tom)	10 GR	10	1	136	root	0.05, 0.06	5201-81 [3]
Spain, (Cadiz), 1981 (Tim tom)	400 EC	9.6	1	136	root	0.01, 0.01	Bayer 1981b 5202-81 [3]
Spain, (Cadiz), 1981 (Tim tom)	400 EC	9.6	1	136	root	0.1, 0.11	5203-81 [3]
Italy, (Latina), 1989 (Delta cuore rosso)	5 GR	10	1	150	root	<0.02, <0.02	Bayer 1988a 0187-88 [4]
Italy, (Latina), 1989 (Delta cuore rosso)	5 GR	10	1	65 85	root	0.045, 0.05 0.041, 0.048	Bayer 1988a 0411-88 [5]
Italy, (Latina), 1995 (Nandor)	10 GR	15	1	90 100 130	root	<0.02, <0.02 <0.02 <0.02, <0.02	Heinemann and Ohs 1997a 501581 [6]
Italy, (Latina), 1995 (Bolero)	10 GR	15	1	90 100 130	root	<0.02, <0.02 <0.02 <0.02, <0.02	506664 [6]
Italy, (Sicily), 1995 (Nelson)	10 GR	15	1	91 100 130	root	<0.02, <0.02 <0.02 0.067, 0.070	506672 [6]
Italy, (Sicily), 1995	10 GR	15	1	90	root	1.19, 0.929 (0.40 *c*)	

Location, year (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
(Junior)				100 131		0.602 (0.19 *c*) 0.093 (0.10 *c*)	506680 [6]
Italy, (Latina), 1996 (Nantes 3 Tip-top)	10 GR	30	1	90 100 130	root	<0.02, <0.02 <0.02 <0.02, <0.02	Heinemann and Ohs 1997b 602752 [7]
Italy, (Latina), 1996 (Bolero F1))	10 GR	30	1	90 100 130	root	<0.02, <0.02 <0.02 <0.02, <0.02	603562 [7]
Italy, (Ferrara), 1996 (Nanthia)	10 GR	30	1	90 100 130	root	<0.02, <0.02 <0.02 <0.02, <0.02	603570 [7]
Italy, (Verona), 1996 (Nentes 5 Sansom)	10 GR	30	1	90 100 131	root	<0.02, <0.02 <0.02 <0.02, <0.02	605589 [7]
Italy, (Sicily), 1997 (Nanco)	10 GR	15	1	90 100 131 143	root	0.023, 0.024 <0.02 <0.02, <0.02 <0.02	Ohs 1998 608572 [8]
Italy, (Sicily), 1997 (Nanco)	5 GR	15	1	90 100 131 143	root	0.027, 0.022 <0.02 <0.02, <0.02 <0.02	608580 [8]
GAP **Australia** **Italy**	 **100 G** **400 liq.** **5 GR**	 **9** **9.6** **15**	 **1** **1** **1**	 **84** **84** **90**			

c Controls.
*Applied 21 days before sowing.
**Applied 7 days before sowing.
[1] Results corrected for recovery; limit of detection 0.01 mg/kg; recovery 79% at 0.5 and 72% at 0.1 mg/kg.
[2] Applied at sowing. Limit of detection = 0.05 mg/kg; recovery with fortification at 0.5 mg/kg = 98%.
[3] Applied 2 days after sowing by spreading and incorporation. Limit of determination = 0.01 mg/kg; recovery at that concentration = 86%.
[4] Applied 10 days before sowing. Limit of determination = 0.02 mg/kg; recovery at that concentration = 87%.
[5] Applied 1 day before sowing. Limit of determination = 0.02 mg/kg; recovery at that concentration = 81%.
[6] Recoveries of fenamiphos 76-87% at 0.02 mg/kg (n = 6); 69-92% at 0.1 mg/kg (n = 11); 74-84% at 1 mg/kg (n = 6).
[7] Limit of determination = 0.02 mg/kg. Recoveries of fenamiphos 71-82% at 0.10 mg/kg (n = 4).
[8] Limit of determination = 0.02 mg/kg. Recovery of fenamiphos 89 and 104% at 0.02 and 73 and 78% at 0.1 mg/kg.

In three of the four Italian trials in 1995, residues in carrots were below the limit of determination. In the fourth however the residues were high and finite levels were found in the control samples. The higher residues were explained as being due to bad weather conditions and the bad condition of the plot. In trial 506680, the average unit weight of the samples was much lower than the average in the other trials: 2-28 g compared with 56-113g, 78-150 g and 14-54 g. The composite sample weights were 1.36 to 2.03 kg in trial 506880, compared to 2.2-2.4 kg, 2.0-3.3 kg and 2.0-2.1 kg in trials 501581, 506664 and 506672. The data from trial 506680 are not considered valid for estimating a maximum residue level or STMR. In the 1997 trials, residues above 0.02 mg/kg were found at day 90 but all later residues were below the limit of determination after treatment at 15 kg ai/ha.

From the 1996 trials it is evident that doubling the application rate still gives fenamiphos residues below the limit of determination in carrots sampled at 90 days or later. These results can be used in the estimation of the maximum residue level and STMR

The residue data are in accord with the findings in the metabolism study of Khasawinah (1973c) where a high proportion of the radioactivity in carrots was present as conjugated derivatives

of fenamiphos phenol sulfoxide and fenamiphos phenol sulfone, neither of which is encompassed by the existing residue definition.

Potatoes. Supervised trials were conducted in Spain and Australia. All results were presented in summary form; in some cases recoveries were not reported. Chromatograms were not provided for any of the trials. The results are shown in Table 68.

Table 68. Residues from supervised trials on potatoes. Tubers analysed.

Location, year (variety)	Application			PHI, days	Residue, mg/kg	Reference
	Form.	kg ai/ha	No.			
Spain (La Puebla), 1975, (Royal Kidney)	5 GR	10	1	118	0.07	Bayer 1975 5200B-75 [1]
Spain (La Puebla), 1977, (Maris Piper)	5 GR	10	1	97 104 111 125	0.17 0.12 0.08 0.04	Bayer 1977 5204-77 [2]
Spain (Mallorca), 1982, (Baris-Bard)	10 GR	10	1	71 92 105	<0.01 <0.01 <0.01	Bayer 1982 5200-82 [3]
Spain (Mallorca), 1982, (Irish Pace)	10 GR	10	1	71 92 105	<0.01 <0.01 <0.01	5201-82 [4]
Australia (WA), 1971, (Delaware)	400 EC	4.47	1	96	<0.05	Bayer Australia 1971b 35/71a [5]
Australia (WA), 1971, (Delaware)	400 EC	8.96	1	96	<0.05	35/71b [6]
GAP **Australia** **Spain**	 **100 G** **400 liq.** **10 GR** **400 EC**	 **10** **5.2** **10** **8-10**	 **1** **1** **1** **1**	 **84** **84** **120** **120**		

[1] Single application by spreading and incorporation; plot size 1700 m^2, sandy loam soil. Samples taken 1 week before harvest. Limit of detection = 0.01 mg/kg; recoveries not reported.
[2] Single application by spreading and incorporation; plot size 1700 m^2, sandy loam soil. Samples taken 2 weeks after harvest. Limit of detection = 0.01 mg/kg; recoveries not reported.
[3] Single application at planting by spreading and incorporation; plot size 50 m^2, sandy soil, pH 7, 1% C. Samples taken at harvest. Limit of detection = 0.01 mg/kg, recovery at 0.05 mg/kg = 94%.
[4] Single application at planting by spreading and incorporation; plot size 25 m^2, sandy soil, pH 7, 3% C. Samples taken at harvest. Limit of detection = 0.01 mg/kg, recovery at 0.05 mg/kg = 94%.
[5] Single application by spraying at 24 hours before planting. Limit of detection 0.01 mg/kg, recovery at 0.1 mg/kg = 78%, recovery at 0.5 mg/kg = 80%. Results corrected for recovery.
[6] Single application by spraying at 24 hours before planting. Limit of detection = 0.01 mg/kg, recovery at 0.1 mg/kg = 95%, recovery at 0.5 mg/kg = 98%. Results corrected for recovery.

The results of trials according to GAP for Australia or Spain ranged from <0.01 to 0.17 mg/kg.

Onions. Trials in Australia and South Africa were reported (Table 70). Field details of the Australian trial were not given.

In the South African trials, Nemacur 400 EC was applied at 3, 4 or 6 kg ai/ha 4 days before sowing onions or at planting. The plot sizes were 600 to 800 m^2. Samples of onion bulbs were taken at maturity. In trial 311/88475/E517 the bulbs were half-developed at the first sampling and fully-developed at the final sampling. The results are shown in Table 69.

Table 69. Fenamiphos residues in onions resulting from supervised trials in Australia and South Africa.

Location, year (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Australia (SA), 1971, (Brown)	43.6% EC	9.7	1	151	mature bulb	<0.01	Bayer Australia 1971c 29/71 [1]
South Africa, (Transvaal) 1990, (Hojem)	400 EC	4	1	139 151 161 172 200	bulb	0.05, 0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05	S. Afr Bur. Stds. 1990a 311/88475/E517 [2]
South Africa, (Western Cape), 1988, (Caledon globe)	400 EC	4	1	78 88 101	bulb	0.05, 0.05 <0.05,<0.05 0.05, 0.05	311/88608/F237 [3]
South Africa, (Western Cape), 1990, (Caledon globe)	400 EC	3 6	1 1	72 81 91 72 81 91	bulb	<0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05	311/88817/G160[4]
GAP **Australia** **South Africa**	 **400 liq.** **400 EC**	 **9.6** **3**	 **1** **1**	 **84** **80**			

[1] Applied to soil by boom spray, then incorporated with tynes and rolled 5 days before sowing. Limit of detection = 0.01 mg/kg; recovery 82% at 0.5 mg/kg, 77% at 0.1 mg/kg; results corrected for recovery.
[2] Limit of detection = 0.05 mg/kg; recovery of fenamiphos = 74%, fenamiphos sulfoxide = 93% and fenamiphos sulfone = 86% at 0.1 mg/kg; results corrected for recovery.
[3] Limit of detection = 0.05 mg/kg; recovery of fenamiphos = 74%, fenamiphos sulfoxide = 93%, fenamiphos sulfone = 86% at 0.1 mg/kg; results corrected for recovery.
[4] Limit of detection = 0.05 mg/kg; recovery of fenamiphos = 82%, fenamiphos sulfoxide = 94%, fenamiphos sulfone = 100% at 0.1 mg/kg.

The trials were at rates in accordance with or in excess of those registered in Australia or South Africa. Results considered acceptable for the estimation of a maximum residue level and STMR are indicated; most results were corrected for recovery. As the samples in the Australian trial were taken later than the specified PHI and field details were not provided, the result was not included in the estimation. In the South African trials, although samples were taken later than the label PHIs, as the crop was mature and the application was either pre-planting or at sowing the trials may be considered to comply with the specified GAP.

Brussels sprouts. Several trials were conducted in the USA; field details were not reported. The registered use pattern for Brussels sprouts in the USA allows a single application equivalent to 6.7 kg ai/ha with no specified PHI. Recoveries by Method 00024/I8 with fortification at 0.01-0.1 mg/kg are reported in Table 61. The results of the trials are shown in Table 70.

Table 70. Residues from supervised trials on Brussels sprouts in the USA.

Location, year, (variety)	Application			PHI, days	Residue, mg/kg	Reference.
	Form.	kg ai/ha	No.			
Washington, 1973 (Jade)	15 GR	10	1	107	0.02	Chemagro 1973a 35889
Virginia, 1973 (Catskill)	15 GR	6.7	1	133	<0.01	35947
California, 1973 (J. Cross)	359 g/l SC	6.7	1	113	<0.01	Chemagro 1973b 35946
Virginia, 1973 (Catskill)	359 g/l SC	6.7	1	133	<0.01	35948
California, 1986 (Lannette)	15 GR	6.7	1	124	<0.01	Mobay 1986a 87382
California, 1986 (Lannette)	15 GR	6.7	1	157	<0.01	87383
California, 1986 (Lannette)	15 GR	6.7	1	157	<0.01	87384
GAP **USA** **Mexico**	 **15 GR** **10 GR**	 **6.7** **3 or 5/season**	 **1** **1**	 **NS** **NS**		

All of the trials except 35889 were at the maximum label rate of 6.7 kg ai/ha and residues were below the limit of determination. Trial 35889 was at 10 kg ai/ha and the PHI was shorter.

Cabbage. Supervised trials were in Australia and the USA. In many cases field details were not given. Recoveries from cabbage in the US trials by Method 00024/I with fortification at 0.05 mg/kg were reported in Table 61. The results of the trials are shown in Table 71.

Table 71. Residues in cabbage from trials in Australia and the USA.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
Australia (WA), 1971 (Comet)	5 GR	8.9	1	106	mature head	<0.01	Bayer Australia 1971d 21/71c [1]
Australia (WA), 1971 (Comet)	5 GR	17.9	1	106	mature head	<0.01	21/71d [1]
Australia (WA), 1971 (Comet)	400 EC	8.9	1	106	mature head	<0.01	Bayer Australia 1971e 21/71a [2]
Australia (WA), 1971 (Comet)	400 EC	17.9	1	106	mature head	<0.01	21/71b [2]
Australia (WA), 1971 (Comet)	400 EC	4.48	1	42	head	<0.01	22/71a [3]
Australia (WA), 1971 (Comet)	400 EC	8.9	1	42	head	<0.01	22/71b [3]
Australia (WA), 1971 (Comet)	400 EC	17.9	1	42	head	0.04	22/71c [3]
USA (Minnesota), 1973 (Golden acre)	15 GR	6.7	1	55	head	0.02	Chemagro 1973c 35890 [4]
USA (Kansas), 1973 (Golden acre)	15 GR	6.7	1	65	head	<0.01	35891 [4]
USA (California), 1973 (Danish boldhead)	15 GR	6.7	1	83	head	<0.01	35892 [4]
USA (Nth Carolina), 1973 (Market prize)	15 GR	10	1	108	head	0.02 (*0.13c*)	35893 [4]
USA (Kansas), 1973 (Golden acre)	15 GR	10	1	65	head	<0.02	35894 [4]
USA (Nth Carolina), 1973 (Market prize)	15 GR	10	1	108	head	0.05	35954 [4]
USA (Nth Carolina), 1973 (Market prize)	15 GR	6.7	1	108	head	<0.01	35955 [4]
USA (Virginia), 1973 (Market prize)	15 GR	6.7	1	84	head	0.02	35956 [4]
USA (Minnesota), 1973 (Golden acre)	3 SC	6.7	1	55	head	0.02	Chemagro 1973d 35895 [4]
USA (Kansas), 1973 (Golden acre)	3 SC	6.7	1	65	head	<0.01	35896 [4]
USA (California), 1973 (Danish boldhead)	3 SC	6.7	1	79	head	0.01	35897 [4]
USA (California), 1973 (Danish boldhead)	3 SC	10	1	79	head	<0.01	35898 [4]
USA (Virginia), 1973 (Market prize)	3 SC	6.7	1	84	head	<0.01	35952 [4]
USA (Nth Carolina), 1973 (Market prize)	3 SC	10	1	108	head	0.02	35953 [4]
USA (Indiana), 1977 (Golden acre)	3 SC	3.7	1	68	head wrapper leaves field trash	<0.01 <0.01 <0.01	Chemagro 1977a 53228 [4]

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
USA (Wisconsin), 1977 (Roundup)	3 SC	2	1	84	head wrapper leaves field trash	<0.01 0.03 0.12	53229 [4]
USA (Indiana), 1977 (Golden acre)	3 SC	3.7	1	68	head wrapper leaves field trash	<0.01 0.01 0.02	53230 [4]
USA (Wisconsin), 1977 (Roundup)	3 SC	3.7	1	84	head field trash	<0.01 0.19	54350 [4]
GAP **Australia** **USA**	 **100 G** **400 liq.** **15 GR**	 **9** **9.6** **6.7**	 **1** **1** **1**	 **NS** **NS** **NS**			

[1] Applied 1 day before transplanting seedlings. Limit of detection = 0.01 mg/kg; recovery = 86% at 1 mg/kg, 84% at 0.5 mg/kg and 80% at 0.1 mg/kg. Area of plot treated = 1.85 m^2; granules distributed by hand then rotary hoed in.
[2] Applied 1 day before transplanting seedlings. Limit of detection = 0.01 mg/kg; recovery = 86% at 1 mg/kg, 84% at 0.5 mg/kg and 80% at 0.1 mg/kg. Area of plot treated = 1.85 m^2; spray applied then rotary hoed in.
[3] Applied at planting. Limit of detection = 0.01 mg/kg; recovery = 86% at 1 mg/kg, 84% at 0.5 mg/kg and 80% at 0.1 mg/kg. Area of plot treated = 0.18 ha; applied by boom spray then rotary hoed in; samples taken 1-2 weeks before normal harvest.
[4] Limit of detection = 0.01 mg/kg.

Registered use patterns in Australia allow a single pre-planting application at 9 or 9.6 kg ai/ha; a PHI is not specified. Only three trials in Australia were in accordance with GAP, as rates in the remaining four trials were either half or twice the maximum label rate. After application at the maximum or twice the maximum rate, the fenamiphos residues in the cabbage heads in all but one of the Australian trials were below the limit of detection.

The registered use pattern for Nemacur 15 GR in the USA allows a single application before or at planting at a rate equivalent to 6.7 kg ai/ha with no specified PHI. The rates in the trials were 0.5, 1 or 1.5 times the maximum rate. The residues in the cabbage heads were below the limit of determination in most of the trials. Wrapper leaves and field trash were also analysed in trials 53228 to 53230 and 54350, where half the GAP rate was applied. Higher residues were found in some of these samples, at levels up to 19 times the residues in the heads. Similar findings were reported in the cabbage metabolism study (Khasawinah, 1973d), where higher levels of radioactivity were present in the outer leaves than in the whole head. The radioactivity was predominantly due to fenamiphos sulfoxide and fenamiphos sulfone.

The data on outer leaves and field trash are useful for estimating any exposure to livestock, which may be fed waste products and non-commercial crop parts after harvest. It was noted that field details were not reported in these trials.

Peppers. Supervised trials were conducted in Italy, Spain and Portugal. The results are shown in Table 72.

In glasshouse trials in Italy and Spain, Nemacur 240 CS (capsule suspension) was applied to pepper plants by drip irrigation (Heinemann and Ohs, 1997c). The product was applied at inflorescence emergence or at fruit development, at a rate equivalent to 10 kg ai/ha. Fruits were sampled at 30/31, 60 and 90 days after treatment. The plot sizes were 40 to 845 m^2 and the soils at all sites were sandy. The pH of the soil was 5.7 and 7.4 in trials 602779 and 603937 respectively, where the soil was covered with black foil and the treatment applied directly to the base of the plants; in trials 603945 and 603953 the product was applied via the irrigation system. The results are shown in Table 72.

In a subsequent set of glasshouse trials in Italy, Spain and Portugal (Blass, 1998a), Nemacur 240 CS was applied by irrigation at a rate equivalent to 10 kg ai/ha. A single application was made to pepper plants at flowering or early fruiting stages and samples were taken 30, 60 and 90 days after

treatment. Plot sizes were 50 to 336 m^2 and at all sites the soil was sandy in the pH range 6-8.4. In the Italian trials, the soil was covered with black plastic foil.

Table 72. Residues in peppers from trials in Italy, Spain and Portugal

Location, year, (variety)	Application			PHI,	Residues,	Reference
	Form.	kg ai/ha	No.	days	mg/kg	
Italy (Lonigo), 1980	5 GR	10 F	1	84	0.05	Bayer 1981c 5205-80 [1]
Italy (Lonigo), 1980	5 GR	10 F	1	84	0.05	5206-80 [1]
Spain (San Javier), 1985 (Gedeon)	10 GR	10 G	1	1 15 29 56 84	<0.05, <0.05 <0.05, <0.05 0.05, 0.1 0.09, 0.1 0.31, 0.35	Bayer 1985a 5208-84 [2]
Spain (Murcia), 1985 (Gedeon)	400 EC	10 G	1	1 15 29 56 85	<0.05, <0.05 0.18, 0.18 0.28, 0.37 0.19, 0.20 0.25, 0.26	Bayer 1985b 5207-84 [3]
Spain (Alicante), 1986 (Gedeon)	400 EC	5 G	2	90 118 153	0.13, 0.17 0.05, 0.06 0.05, 0.05	Bayer 1986a 5203-86 [4]
Italy (Sabaudia), 1987 (Eldor)	5 GR	14.4 F	1	65 81	<0.02, <0.02 <0.02, <0.02	Bayer 1987a 5224-87 [5]
Spain (Alicante), 1987 (Lamuyo)	10 GR	10 F	1	63	<0.05, <0.05	Bayer 1987b 5235-87 [6]
Spain (Semillas Llad), 1987, (Hungaro)	10 GR	10 F	1	75	0.06, 0.06	5236-87 [7]
Spain (Alicante), 1987, (Lamuyo)	400 EC	10 F	1	50	0.08, 0.08	Bayer 1987c 5217-87 [8]
Spain (Semillas Llad), 1987 (Hungaro)	400 EC	10 F	1	75	0.05, 0.06	5218-87 [9]
Italy (Latina), 1996, (Sonar)	240 CS	10 G	1	30 60 90	0.119, 0.108 <0.02, <0.02 <0.02	Heinemann & Ohs 1997c 0277-96 [10]
Italy (Ragusa), 1996, (Lux)	240 CS	10 G	1	31 60 90 (green) 90 (yellow)	0.041, 0.033 <0.02, <0.02 <0.02 <0.02	0393-96 [10]
Spain (Almeria), 1996 (Anibal)	240 CS	10 G	1	31 60 90	0.067, 0.071 0.02, 0.02 <0.02	0394-96 [10]
Spain (Almeria), 1996 (Drago)	240 CS	10 G	1	31 60 90	0.187, 0.177 0.07, 0.064 <0.02	0395-96 [10]
Italy (Latina), 1997, (Gordo)	240 CS	10 G	1	30 60 90	<0.02, <0.02 <0.02, <0.02 <0.02	Blass 1998a 0099-97 [11]
Italy (Ragusa), 1996, (Soldi)	240 CS	10 G	1	30 60 90	0.091, 0.088 0.110, 0.096 <0.02	0558-97 [11]
Spain (Almeria), 1996 (Roldan)	240 CS	10 G	1	30 60 90	<0.02, <0.02 <0.02, <0.02 <0.02	0559-97 [11]
Portugal (Lissabon), 1997, (Sonar)	240 CS	10 G	1	30 60 90	0.306, 0.287 0.80, 0.065 <0.02	0560-97 [11]
GAP **Spain**	**10 GR**	**5-10**	**1**	**90**		
	400 EC	**5-10**	**1**	**90**		

F: field G: glasshouse

[1] Field trial. Limit of determination = 0.05 mg/kg; recoveries not indicated. Treatment applied 20 days before planting. Plot size = 10 m^2.

[2] Glasshouse trial; single application by spreading by hand and incorporation in soil followed by irrigation; applied at the fruiting stage; plot size = 112 m^2; soil pH 7.5; loamy soil, 1% C. Recovery = 100% at 0.1 mg/kg. Limit of determination = 0.05 mg/kg.

[3] Glasshouse trial; single application by drip irrigation; applied at the fruiting stage; plot size = 36 m^2; soil pH 7.5; loamy sand, 1% C; recovery = 100% at 0.1 mg/kg. Limit of determination = 0.05 mg/kg.

[4] Glasshouse trial; 2 applications by drip irrigation, 1st at planting and 2nd 14 days after planting; plot size = 36 m^2; pH 7.5-8.0; sandy soil 1% C; recovery = 82% at 0.1 mg/kg, 95% at 0.01 mg/kg. Limit of determination = 0.05 mg/kg.

[5] Field trial; single application 11 days after planting by spreading; plot size = 3000 m^2 (0.3 ha); sandy soil; irrigation every 8-10 days by sprinkler. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 103%.

[6] Field trial; single application in-furrow at planting with slight incorporation; plot size = 100 m^2; sandy soil pH 7.5, 2% C. Limit of determination = 0.05 mg/kg; recovery at 0.05 mg/kg = 70%.

[7] Field trial; single application at sowing by spreading and incorporation; plot size = 10 m^2; sandy soil pH 7, 1% C. Limit of determination = 0.05 mg/kg, recovery at 0.05 mg/kg = 70%.

[8] Field trial; single application 13 days after planting (8-leaf stage) by drench spray; plot size = 100 m^2; sandy soil pH 7.5, 2% C. Limit of determination = 0.05 mg/kg, recovery at 0.05 mg/kg = 70%.

[9] Field trial; single application at sowing by spraying and incorporation; plot size = 10 m^2; sandy soil pH 7, 1% C. Limit of determination = 0.05 mg/kg, recovery at 0.05 mg/kg = 70%.

[10] Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg 79-100% (n = 6), recovery at 0.1 mg/kg 76-94% (n = 10), recovery at 1 mg/kg 83-94% (n = 6).

[11] Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 81, 86%, recovery at 0.1 mg/kg 75-93% (n = 5).

The trials with the GR and EC products can be compared with registered use patterns in Spain, which allow a single pre-planting application at a maximum rate of 10 kg ai/ha and a PHI of 90 days. In both field and glasshouse trials fenamiphos residues 90 days after treatment were <0.02-0.06 mg/kg, after application at sowing. In trials where the application was made after planting, at flowering or early fruiting, higher residues in the range 0.25-0.35 mg/kg were present 84 or 85 days after treatment. As the specified GAP for the 400 EC product indicates application before sowing or at transplanting these results may not provide an accurate indication of likely residues after treatment at an early stage, but they give an indication of residues that may occur after late application.

The results with the 240 CS formulation are included although registration of the product is pending and only draft labels were provided.

Tomatoes. Numerous supervised trials were conducted in Australia, Brazil, South Africa, Spain, Italy and Portugal. The formulations used included 5 and 10 GR, 400 EC, 250 EW and 240 CS. The results are shown in Table 73. The trials by Heinemann and Ohs and by Blass (below) were conducted and reported in accordance with GLP. For the other trials, where only data sheets were provided, the relevant details are given as footnotes to the Table.

Glasshouse trials on tomatoes were conducted in Italy, Portugal and Spain (Heinemann and Ohs, 1997d). Nemacur 240 CS (capsule suspension) was applied by drip irrigation at a rate equivalent to 10 kg ai/ha at pre-flowering (inflorescence emergence) and fruit development. Fruit were sampled 60 or 61 days after treatment. The plot sizes at the four sites were 34 to 530 m^2 and the soils were sandy with the pH at two sites 5.7 and 7.7, 0.4 and 0.5% C. In trials 602787 and 603848 the soil surface was covered with black foil; in trial 603864 the upper parts of the plant were cut.

In subsequent glasshouse trials (Blass, 1998b) Nemacur 240 CS was applied by drip irrigation at a rate equivalent to 10 kg ai/ha in three trials and at 9.4 in one trial owing to underdosing. The trials were in Italy, Portugal and Spain, with applications 21, 87, 76 and 44 days after planting in trials 700460, 705616, 705624 and 705632 respectively. Plot sizes were 8.5-525 m^2. The soils were typically sand, sandy loam or loamy sand, with pH 5.5-7.8 and 0.5-2.2% C.

Table 73. Residues in tomatoes from supervised trials in Australia, Brazil, Italy, Portugal, South Africa and Spain.

Location, year, (variety)	Application			PHI,	Residues,	Reference
	Form.	kg ai/ha	No.	days	mg/kg	
Australia (QLD), 1971 (Grosse lisse)	5 GR	11.2 F	1	78	<0.05	Bayer Australia 1971f 11/71d [1]
Australia (QLD), 1971 (Grosse lisse)	400 EC	8.9 F	1	81	<0.05	Bayer Australia 1971g 11/71a [2]
Australia (QLD), 1971 (Grosse lisse)	400 EC	11.2 F	1	81	<0.05	11/71 b [2]
Australia (QLD), 1971 (Grosse lisse)	400 EC	13.4 F	1	81	<0.05	11/71c [2]
Australia (SA), 1971 (Grosse lisse)	400 EC	8.7 F	1	127 161	0.15 <0.05	12/71a [3]
Australia (SA), 1971 (Grosse lisse)	400 EC	8.7 F	1	127 161	<0.05 <0.05	12/71b [3]
Brazil (Agrocica), 1985	10 GR	2 F	1	124	<0.1	Fundacao C. & T 1985 BRA-78900-85A [4]
Brazil (Sao Paulo), 1989 (Santa Cruz-Okada)	10 GR	5 F	1	70 94	<0.1 <0.1	U. Sao Paulo 1989 BRA-LYPES89-1-A [5]
Brazil (Sao Paulo), 1989 (Santa Cruz-Okada)	10 GR	10 F	1	94	<0.1	BRA-LYPES89-1-B [5]
South Africa, 1976	10 GR	10 F	1	58 73 88	<0.05 <0.05 <0.05	S. Afr. Bur. Stds 1977 311/880/P163 [6]
South Africa, 1976	400 EC	10 F	1	58 73 88	<0.05 <0.05 <0.05	
South Africa, 1984 (Hibberdene)	10 GR	1 g ai /m, 30 cm band F	1	86 99 112	0.30 0.14 0.10	S. Afr. Bur. Stds 1985 311/88694/B40 [7]
	10 GR + 400 EC	0.5 g/m 30 cm or 40 cm band	1 + 1	35 48 61	0.36 0.25 0.16	
	400 EC	1 g ai/m, 30 cm band	1	86 99 112	0.17 0.14 0.06	
	250 EW	1 g ai/m, 30 cm band	1	86 99 112	0.12 0.09 0.06	
	400 EC	1 g ai/m 30 cm band + 0.5 g ai/m 40 cm band	1 + 1	35 48 61	0.15 0.07 0.11	
	400 EC	1 g ai/m 30 cm band + 0.5 g ai/m	1 + 1*	0 7 13 20 33	<0.05 0.10 <0.05 <0.05 <0.05	
Spain (Alicante), 1984 (Restino)	400 EC	10 G	1	1 15 29 62	<0.05, <0.05 0.33, 0.41 0.33, 0.37 0.19, 0.27	Bayer 1985c 5206-84 [8]
Spain (San Javier), 1986 (Carmelo)	400 EC	5 G	2	55 84 112	0.1, 0.13 <0.01, 0.01 <0.01, <0.01	Bayer 1986b 5202-86 [9]
Spain (Moreno), 1988 (A-7)	400 EC	10 F	1	60	<0.02, <0.02	Bayer 1988b 0077-88 [10]
Spain (St. Boi de Llobregat, (1988) (A-7)	10 GR	10 F	1	60	<0.02, <0.02	Bayer 1989a 0075-88 [11] F
Spain (Sr. Jordana), 1988 (Carmelo)	10 GR	10 F	1	66	<0.02, <0.02	0076-88 [12]
Spain (El Masnou), 1988 (Carmelo)	400 EC	10 F	1	66	<0.02, <0.02	Bayer 1989b 0078-88 [13]

Location, year, (variety)	Application			PHI,	Residues,	Reference
	Form.	kg ai/ha	No.	days	mg/kg	
Italy (Latina), 1996 (Sidonia)	240 CS	10 G	1	30 60 90	0.381, 0.368 0.02, 0.02 <0.02	Heinemann & Ohs 1997d 0278-96 [14]
Italy (Sicily), 1996 (Felicia)	240 CS	10 G	1	31 60 90	0.081, 0.070 <0.02, <0.02 <0.02	0384-96 [14]
Portugal (Lissabon), 1996 (Indalo)	240 CS	10 G	1	50 61 70	<0.02, <0.02 <0.02, <0.02 <0.02	0385-96 [14]
Spain (Almeria), 1996 (Garbo)	240 CS	10 G	1	32 60 90	0.066, 0.070 0.092, 0.080 0.042	0386-96 [14]
Italy (Latina), 1997 (Arletta)	240 CS	10 G	1	30 60 90	<0.02, <0.02 <0.02, <0.02 <0.02	Blass 1998b 0046-97 [15]
Italy (Ragusa), 1997 (Cencara)	240 CS	10 G	1	30 60 90	0.079, 0.081 <0.02, <0.02 <0.02	0561-97 [15]
Spain (Barcelona), 1997 (Alboran)	240 CS	9.4 G	1	31 60 90	0.205, 0.167 0.142, 0.144 0.032	0562-97 [15]
Portugal (Lissabon), 1997 (Indalo)	240 CS	10 G	1	30 60 90	<0.02, <0.02 <0.02, <0.02 <0.02	0563-97 [15]
GAP						
Australia	**100 G**	**11**	**1**	**NS**		
	400 EC	**9.6**	**1**	**NS**		
Brazil	**10 GR**	**3-4**	**1**	**90**		
Italy	**5 GR**	**10-15**	**1**	**20**		
Portugal	**10 GR**	**3.4**	**1**	**90**		
	400 EC	**3.2**	**1**	**90**		
South Africa	**10 GR**	**1 g ai/m**	**1**	**NS**		
	400 EC	**1 g ai/m**	**1**	**NS**		
Spain	**10 GR**	**5-10**	**1**	**90**		
	400 EC	**5-10**	**1**	**90**		

F: field G: glasshouse

* Second treatment applied 1 week before harvest.

[1] Scattered by hand to soil 3 days after transplanting; left on surface. Limit of detection = 0.05 mg/kg; recovery at 1 mg/kg = 72%, recovery at 0.5 mg/kg = 69%.

[2] Applied by boom to soil 1 day before transplanting and rotary hoed in. Limit of detection = 0.05 mg/kg; recovery at 1 mg/kg = 72%, recovery at 0.5 mg/kg = 69%.

[3] Applied by boom spray 21 days before transplanting. Limit of detection = 0.05 mg/kg; recovery at 1 mg/kg = 72%, recovery at 0.5 mg/kg = 69%. Hot dry weather, little rainfall, regular irrigation.

[4] Applied at planting by spreading; no recovery data given.

[5] Field trial with spreading at transplanting. Plot size = 12 m^2, clay soil, pH 5.7 % C = 1.8. Limit of determination = 0.1 mg/kg, recovery at 0.1 mg/kg 83-87%.

[6] No field details given; limit of detection = 0.05 mg/kg. Recoveries for fenamiphos sulfone and sulfoxide conducted at 1 mg/kg = 98% fenamiphos sulfone and 92% for fenamiphos sulfoxide.

[7] No field details given; limit of detection = 0.05 mg/kg. Mean recoveries at 0.1 mg/kg = 104% for fenamiphos, 94% fenamiphos sulfone and 96% fenamiphos sulfoxide. All results corrected for recovery.

[8] Glasshouse trial. Applied by drip irrigation at fruit development stage. Plot size = 55 m^2 Loamy clay soil pH 7.5, % C = 0.53. Recovery = 100% at 00.1 mg/kg.

[9] Glasshouse trial. Product applied 28 and 42 days after planting; last application at fruit development. Trial plot 30 m^2. Loamy sand soil pH 7.5-8, % C = 0.53. Limit of determination = 0.01 mg/kg, recovery at 0.01 mg/kg = 101%, at 0.1 mg/kg = 96%.

[10] Field trial. Applied by drip irrigation at 31 days after planting, flowering stage. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 91%. Plot size 12.8 m^2, sandy soil pH 6.5.

[11] Field trial. Applied by spreading at 30 days after transplanting at flowering stage. Plot size = 12.8 m^2, sandy soil type pH 6.5. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 91%.

[12] Field trial. Single application by spreading at 6 days after transplanting. Plot size = 45.5 m^2, sandy soil pH 7.5 % C = 2. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 91%.

[13] Field trial. Single application by drip irrigation 6 days after planting. Plot size = 53.8 m^2, sandy soil pH 7.5, 2% C. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 91%.
[14] Glasshouse trials. Single application by drip irrigation 6 to 49 days after planting. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 87, 88%, recovery at 0.1 mg/kg 72-102% (n = 6), recovery at 1 mg/kg = 73, 79%.
[15] Glasshouse trials. Single application by drip irrigation at 21-87 days after planting. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 95, 97%, recovery at 0.1 mg/kg 75-90% (n = 7).

and those with the CS formulation ranged from <0.02 mg/kg to 0.3 mg/kg, predominantly from field trials. In all trials except the South African trials and one CS glasshouse trial (705624), fenamiphos residues were below the limit of determination. Residues of 0.06 to 0.36 mg/kg were found in some of the trials in South Africa at various harvest intervals.

Zucchini. In a glasshouse trial in Italy Nemacur 240 CS (capsule suspension) was applied by drip irrigation to plants at the 3 to 5 leaf stage. The product was applied at a rate equivalent to 10 kg ai/ha directly to the base of each plant. Drip irrigation was used to water the plants. Plot sizes were 40 to 79 m^2. The soils in all the glasshouses were sandy, with a pH range of 5.7 to 8.1. In trials R602795 and R603988 the soil was covered with a black material. The results are shown in Table 74. Recoveries from zucchini by method 00024/I8 were reported in the modification M003 to M002 (Blass, 1997a,b) described above.

Table 74. Residues in zucchini from trials in Italy with Nemacur 240 CS

Location, year, (variety)	Application			PHI,	Residues,	Reference
	Form.	kg ai/ha	No.	days	mg/kg	
Latina, 1996 (President)	240 CS	10	1	30 60 90	0.037, 0.034 <0.02, <0.02 <0.02	Heinemann & Ohs 1997e 0279-96 [1]
Ragusa, 1996 (Stor-green)	240 CS	10	1	30 60 90	<0.02, <0.02 <0.02, <0.02 <0.02	0396-96 [1]
Latina, 1996 (President)	240 CS	10	1	30 60 90	<0.02, <0.02 <0.02, <0.02 <0.02	0398-96[1]
Ragusa, 1996 (Stor-green)	240 CS	10	1	30 60 90	0.107, 0.090 <0.02,<0.02 <0.02	0399-96[1]
GAP **Spain (cucurbits)**	**10 GR** **400 EC**	**10** **10**	**1** **1**	**90** **90**		

[1] Limit of determination = 0.02 mg/kg; recovery at 0.02 mg/kg 85-110% (n = 3), at 0.1 mg/kg 75-112% (n = 6), at 1 mg/kg = 85, 87%.

Fenamiphos was found at levels above the limit of determination at 30 days in two trials (602795 and 603996). This was explained as being due to cold temperatures in the glasshouses in trials 603996 and 603961, resulting in retarded fruit growth and smaller fruits. This may be a factor but the average unit weights in 603961 were lower than those in 603996 and the residues were below the LOD. Black cloth covered the soil surface in trial 602795 which may have contributed to the finite residues at day 30.

Melons. Supervised trials in Australia, Brazil, Guatemala, Mexico and Italy were reported. The results are shown in Table 75.

Four trials were conducted at each of two sites, Coahuila and Durango, in Mexico. Nemacur 15 GR was applied to the soil in-furrow at planting at 3 kg ai/ha (Leslie, 1988a). Fruit were collected 62 or 64 days after planting and residues were determined in the pulp and peel and expressed on a whole fruit basis. Plots were 200 m^2, predominantly composed of clay or sandy soils with pH 6.5-7.5. Residues in the whole fruit were below the limit of determination of 0.05 mg/kg.

In glasshouse trials on melons in Italy (Heinemann and Ohs, 1997f) at four sites, Nemacur 240 CS was applied at a rate of 10 kg ai/ha by drip irrigation 20-36 days after planting. Plots were 40-61 m^2 and were composed of sand or sandy loam soils at pH 5.7-8. At all sites the soil was covered by black foil. Samples were taken at 50, 59/60 and 90 days after treatment. Residues were determined in the whole fruit and pulp.

In subsequent glasshouse trials in Italy (Blass, 1998c) Nemacur 240 CS was applied to five test sites at times from 1 to 65 days after planting. The growth stages ranged from four-leaf to flowering. The product was applied by drip irrigation at a rate equivalent to 10 kg ai/ha. Plot sizes were 66 to 82 m^2 and soils were typically clay sand or sandy loam, pH 7.5 to 8.5, and 0.6-1.7% C. In trials 700452, 705543 and 705551 the soil was covered with black foil. Samples of whole fruit were collected 50, 60/61 and 67/70 days after treatment; pulp was analysed in addition to whole fruit.

Table 75. Residues of fenamiphos in melons from trials in Australia, Guatemala, Mexico and Italy.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
Guatemala (Zacapa), 1987 (Mayan sweet)	10 GR	10	1	85	fruit	≤0.05	Bayer 1987d GUA-36-87-A [1] F
Guatemala (Zacapa), 1987 (Mayan sweet)	10 GR	10	1	71	fruit	≤0.05	Bayer 1987d GUA-36-87-B [1] F
Guatemala (Zacapa), 1987 (Mayan sweet)	10 GR	4	1	85	fruit	≤0.05	Bayer 1987d GUA-36-87-C [1] F
Guatemala (Zacapa), 1987 (Mayan sweet)	10 GR	4	1	71	fruit	≤0.05	Bayer 1987d GUA-36-87-D [1] F
Mexico (Durango), 1983 (Sierra gold)	15 GR	3	1	64	pulp peel whole fruit	≤0.01 <0.01 ≤0.01	Leslie 1988a 96784
Mexico (Durango), 1983 (Sierra gold)	15 GR	3	1	64	pulp peel whole fruit	≤0.01 <0.01 ≤0.01	
Mexico (Coahuila), 1983 (Imperial 45)	15 GR	3	1	62	pulp peel whole fruit	≤0.01 <0.01 ≤0.01	
Mexico (Coahuila), 1983 (Imperial 45)	15 GR	3	1	63	pulp peel whole fruit	≤0.01 0.02 ≤0.01	
Italy (Porgo Piave), 1989 (Charantes)	5 GR	15	1	85 100 105	pulp peel whole fruit pulp peel whole fruit pulp peel whole fruit	≤0.02 <0.02 ≤0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	Bayer 1990a 0064-89 [3] F
Australia (QLD), 1971 (Hales best)	400 EC	8.9	1	112	mature fruit	≤0.01	Bayer Australia 1971h 33/71a [4] F
Australia (QLD), 1971 (Hales best)	400 EC	8.9	1	77	mature fruit	≤0.01	33/71b [5] F
Brazil (Sao Paulo), 1995 (Valenciano)	400 EC	4	1	90	whole fruit	≤0.02	U. Sao Paulo 1996 BRA-2009-96-A [6] F
Brazil (Sao Paulo), 1995 (Valenciano)	400 EC	8	1	90	whole fruit	<0.02	BRA-2009-96-B [6] F
Italy (Latina), 1996, (Proteo)	240 CS	10	1	50 60 90	whole fruit	0.041, 0.042 <0.02, <0.02 <0.02	Heinemann and Ohs 1997f 0281-96 [7] G

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
				50 60 90	pulp	<0.02, <0.02 <0.02, <0.02 <0.02	
Italy (Ravenna), 1996, (Drake)	240 CS	10	1	50 60 90 50 60 90	whole fruit pulp	0.034, 0.036 0.02, 0.021 <0.02 0.022, 0.021 <0.02, <0.02 <0.02	0376-96 [7] G
Italy (Latina), 1996, (Mambo)	240 CS	10	1	50 60 90 50 60 90	whole fruit pulp	<0.02, <0.02 <0.02, <0.02 <0.02 <0.02, <0.02 <0.02, <0.02 <0.02	0377-96 [7] G
Italy (Verona), 1996, (Golden Star)	240 CS	10	1	50 59 80 90 50	whole fruit pulp	0.046, 0.044 0.025, 0.028 <0.02 <0.02 0.021, 0.025	0378-96 [7] G
				59 80 90		<0.02, <0.02 <0.02 <0.02	
Italy (Verona Sth), 1997, (Super market)	240 CS	10	1	50 60 70 50 60 70	whole fruit pulp	0.03 <0.02 <0.02 0.03 <0.02 <0.02	Blass 1998c 0045-97 [8] G
Italy (Verona Sth), 1997, (Super market)	240 CS	10	1	50 61 70 50 61 70	whole fruit pulp	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0554-97 [8] G
Italy (Ravenna), 1997, (Drake)	240 CS	10	1	60 70 60 70	whole fruit pulp	<0.02 <0.02 <0.02 <0.02	0555-97 [8] G
Italy (Ravenna), 1997, (Crido)	240 CS	10	1	50 60 67 50 60 67	whole fruit pulp	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0557-97 [8] G
Italy (Ravenna Nth), 1997	240 CS	10	1	50 60 70	whole fruit	0.03 <0.02 <0.02	0801-97 [8] G

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
				50 60 70	pulp	0.03 <0.02 <0.02	
GAP **Australia** **Brazil** **Guatemala** **Italy** **Spain** 	 **400 liq.** **400 EC** **10 GR** **12 GR** **15 GR** **5 GR** **10 GR** **400 EC**	 **9.6** **4** **2.5-5** **0.72-1.2** **2.5-5.1** **10-15** **10** **10**	 **1** **1** **1** **1** **1** **1** **1** **1**	 **NS** **NS** **60** **60** **60** **20** **90** **90**			

F: field G: glasshouse

[1] Field trial. Single application by spreading and incorporation at sowing or 14 days before sowing. Plot size 552 m^2. Soil type described as "Franco-arenoso" pH 6.7, 1.85% C. Limit of determination = 0.05 mg/kg, recovery at 0.05 mg/kg = 68%.

[2] Field trials. Recovery at 0.05 mg/kg = 102, 88, 76% from pulp, 88, 88, 90% from peel for F, FSO and FSO_2 respectively. Recoveries of fenamiphos were 89 and 109% at 0.1 and 0.5 mg/kg from pulp and 87% at 0.5 mg/kg from peel. Limit of determination = 0.05 mg/kg. All chromatograms provided.

[3] Field trial. Single application at 18 days before planting by spreading. Plot size = 100 m^2, sandy soil pH 7, 1.53% C. Limit of determination = 0.02 mg/kg, recovery from pulp = 88% at 0.02 mg/kg.

[4] Applied by boom spray and incorporated with rotary hoe 35 days before sowing. Limit of detection = 0.01 mg/kg, recovery at 0.1 and 0.5 mg/kg = 73% and 78% respectively.

[5] Applied by boom spray and incorporated with rotary hoe 4 days before sowing. Limit of detection = 0.01 mg/kg, recovery at 0.1 and 0.5 mg/kg = 73% and 78% respectively.

[6] Field trial. Applied by spraying at planting. Loamy sand soil pH 5.9, 1.3% C. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg 86-98%.

[7] Glasshouse trial. Limit of determination = 0.02 mg/kg, recovery of fenamiphos at 0.02 mg/kg 82-93% (n = 6), at 0.1 mg/kg 75-91% (n = 14), at 1 mg/kg 78-89% (n = 6).

[8] Glasshouse trial. Limit of determination = 0.02 mg/kg. Recovery from whole fruit = 92% at 0.02 mg/kg, 76-92% at 0.1 mg/kg (n = 5). Recovery from pulp = 88% at 0.02 mg/kg, 72-92% at 0.1 mg/kg (n = 5).

There were 13 field and 9 glasshouse trials. The residues in the trials according to GAP in Australia, Brazil and Guatemala were all below the limit of determination, both in pulp and whole fruit. In the trials in Mexico according to GAP in Guatemala, fenamiphos residues in the pulp and whole fruit were all below the limit of determination. The underlined residues were used in the estimation of the maximum residue levels and the double-underlined residues in the estimation of the STMR for the edible portion.

After treatment with the CS product the residues in the whole fruit were below the limit of determination in all but one trial (603783) where levels of 0.025 and 0.028 mg/kg were found in whole fruit, although residues in the pulp were <0.02 mg/kg.

Watermelons. Results from trials in Italy were in summary form. Fenamiphos residues were determined in the pulp, peel and whole fruit. The results are shown in Table 76. Recoveries from watermelons were reported in supplement E022 (Ohs, 1988b) to method 00024/I8 as 93% at 0.02 mg/kg and 87% at 0.1 mg/kg.

Table 76. Residues in supervised trials on watermelons in Italy.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Latina, 1988, (Crimson Sweet)	5 GR	10	1	99 109	fruit	<u>≤0.02</u>, <0.02 <0.02, <0.02	Bayer 1989c 0197-88 [1] F
Borgo Piave, 1989, (Crimson Sweet)	5 GR	15	1	85 100 105 85	pulp peel	<u>≤0.02</u>, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02	Bayer 1990b 0062-89 [2] F

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
				100 105 85 100 105	whole fruit	<0.02, <0.02 <0.02, <0.02 <0.02 <0.02 <0.02	
GAP **Italy (melon)** **Spain**	**5 GR** **10 GR**	**10-15** **5-10**	**1** **1**	**20** **90**			

[1] Single application by spreading 20 days before planting. Plot size = 100 m^2, sandy soil, pH 7, 1.53% C. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg = 93%.
[2] Single application by spreading 2 days before planting. Plot size = 200 m^2, sandy soil, pH 7, 1.53% C. Limit of determination = 0.02 mg/kg, recovery at 0.02 mg/kg from pulp and peel = 88% (n = 3).

Although the Italian label provided does not specifically refer to use on watermelon, the use pattern on melons was taken as relevant GAP. The trials in Italy were also compares with registered uses in Spain. After a single application of fenamiphos at 10 or 15 kg ai/ha, residues in the whole fruit, pulp and peel were below the limit of determination 85 days after treatment.

Citrus fruit

Grapefruit. Data from trials in the USA are shown in Table 77. The results were in the form of summary sheets with chromatograms. In early trials (1972), residues were determined in the whole fruit and in later work (1981) the residues were determined in the pulp and peel and in the whole fruit. Recoveries at a fortification level of 0.1 mg/kg were reported in Table 61.

Table 77. Residues from supervised trials on grapefruit in the USA.

Year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
Arizona, 1972	15 GR	33.6	1	184	fruit	<0.01	Chemagro 1972a 33085 [1]
Texas, 1972	15 GR	33.6	1	183	peel pulp	<0.01 <0.01	33086 [1]
Florida, 1972	15 GR	33.6	1	184	fruit	<0.01	33147 [1]
Arizona, 1972	3 SC	33.6	1	184	fruit	<0.01	Chemagro 1972b 33075 [2]
Florida, 1972	3 SC	33.6	1	186	fruit	0.5, 0.56	33082 [2]
California, 1981 (Marsh)	15 GR	33.6	1	30 60 126 182 30 60 126 182 30 60 126 182	peel pulp whole fruit 	0.02 0.05 0.06 0.02 <0.01 <0.01 <0.01 <0.01 <0.01 0.02 0.02 <0.01	Mobay 1981a 69914 [3]
Texas, 1981, (Ruby Red)	15 GR	33.6	1	30 59 124 169 30 59 124	peel pulp 	0.01 0.01 0.02 0.04 <0.01 <0.01 <0.01	69915 [4]
				169 30 59 124 169	 whole fruit 	<0.01 <0.01 <0.01 <0.01 0.01	

Year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Florida, 1981, (Marsh Seedless)	15 GR	33.6	1	30 61 122 184 243 30 61 122 184 243 30 61 122 184 243	peel pulp whole fruit 	0.24 0.43 0.73 0.80 0.25 0.03 0.05 0.08 0.03 <0.01 0.09 0.13 0.28 0.29 0.12	69916 [5]
California, 1981, (Marsh)	360 SC	33.6	1	30 60 126 182 30 60 126 182 30 60 126 182	peel pulp whole fruit 	0.07 0.14 0.22 0.05 0.02 0.02 0.01 <0.01 0.04 0.06 0.09 0.02	Mobay 1981b 69917 [6]
Texas, 1981, (Ruby Red)	360 SC	33.6	1	30 59 124 169 30 59 124 169 30 59 124 169	peel pulp whole fruit 	0.02 0.03 0.03 0.01 0.01 <0.01 <0.01 <0.01 0.01 0.02 0.01 <0.01	69918 [7]
Florida, 1981, (Marsh Seedless)	360 SC	33.6	1	30 61 122 184 243 30 61 122 184 243 30 61 122 184 243	peel pulp whole fruit 	0.30 0.13 0.43 0.68 0.28 0.03 0.03 0.04 0.03 0.02 0.11 0.05 0.15 0.26 0.09	66919 [8]
GAP for citrus fruit	**350 EC**	**5-8.4**	**1**	**30**			

[1] Single broadcast application (within dripline).
[2] Single application by soil drench (within dripline).
[3] Single application by surface broadcast; plot size = 144 m^2; growth stage at application 50 mm fruit.
[4] Single broadcast application; plot size = 222.8 m^2; growth stage at application ½-grown green fruit.
[5] Single surface broadcast application; plot size = 44 m^2; growth stage at application ¼ to ½-grown green fruit.
[6] Single application by surface broadcast; plot size = 573.4 m^2; growth size at application 50 mm fruit.
[7] Single application by surface broadcast; plot size = 222.8 m^2; growth stage at application ½-grown green fruit.
[8] Single application by surface broadcast; plot size = 44 m^2; growth stage at application ¼ to ½-grown green fruit.

All trials were at 4 times the maximum registered use rate in the USA, so the results could not be used to estimate mean or maximum levels. Residues in the whole fruit 30 days after treatment were <0.01-0.11 mg/kg, and in pulp and peel <0.01-0.03 mg/kg and <0.01-0.3 mg/kg respectively. Overall, residues in the edible portion (pulp) were lower than in the whole fruit or peel.

Lemons. Data were provided from trials in Australia, South Africa and the USA. Recoveries at 0.02 and 0.05 mg/kg from both pulp and peel were reported in Table 61.

Table 78. Results of trials on lemons in the USA and South Africa.

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	or report no.
USA (Arizona), 1972	360 SC	33.6	1	184	fruit	0.01	Chemagro 1972c 32936[1]
USA (Arizona), 1976, (Feminello)	15 GR	33.6	1	190	peel pulp whole fruit	0.32 0.01 0.18	Chemagro 1976a 47143 [2]
USA (Arizona), 1976, (Feminello)	360 SC	33.6	1	190	peel pulp whole fruit	1.15 0.05 0.44	Chemagro 1976b 47140 [3]
Australia, 1980, (Eureka)	436 g/l	40	1	8	fruit	<0.02	Bayer Australia 1980a 21/80 [4]
USA (California), 1986,	15 GR	22.4	1	31	pulp	<0.01	Mobay 1986b
(Eureka)				80 129 185 264 349 31 80 129 185 264 349 31 80 129 185 264 349	 peel whole fruit 	<0.01 <0.01 <0.01 <0.01, <0.01 <0.01 <0.01 <0.01 0.01 <0.01 0.02, 0.01 <0.01 <0.01 <0.01 <0.01 <0.01 0.01, <0.01 <0.01	91359 [5]
USA (California), 1986, (Eureka)	360 EC	22.4	1	31 80 129 185 264 264 349 31 80 129 185 264 264 349 31 80 129	pulp peel whole fruit 	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 0.08 0.01 <0.01 <0.01 <0.01 0.02 <0.01 0.03 <0.01 <0.01	Mobay 1986c 91358 [6]
				185 264 264 349	 	<0.01 <0.01 <0.01 <0.01	

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	or report no.
South Africa (Nelspruit), 1989	10 GR	2.5 g ai/m^2	1	60 100 120 150 60 100 120 150	pulp peel 	<0.05, 0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 0.08, 0.08 0.05, 0.05 <0.05, <0.05 <0.05, <0.05	311/88812/G155 [7]
GAP **Australia** **South Africa** **USA (for citrus fruit)**	 **400 liq.** **10 GR** **350 EC**	 **30** **12 or 2 g ai/m^2** **5-8.4**	 **1** **1**	 **NS** **150** **30**			

[1] Single application by soil drench (within dripline).
[2] Single application by soil broadcast, raked into soil within 1 day of application; growth stage at application: fruit set.
[3] Single application by soil broadcast (within dripline), raked in within 1 day after application; growth stage at application: fruit set.
[4] Limit of detection = 0.02 mg/kg, recovery at 0.1 mg/kg = 90%.
[5] Single application by soil broadcast incorporation into the ground; growth stage at application mature fruit; sandy soil, pH 6.5-7.5, <1% C.
[6] Single application by soil broadcast incorporation into the ground; growth stage at application mature fruit; sandy soil, pH 6.5-7.5, <1% C.
[7] Single application by spreading by hand at flowering stage; area treated 62.5 m^2, sandy loam soil, pH 5.2, 1-2% C, Limit of detection = 0.05 mg/kg, recovery at 0.1 mg/kg = 98, 103, 65% of F, FSO and FSO_2 respectively from pulp, 76, 80 and 105% from peel.

The trials on lemons were also at 2.6 or 4 times the maximum registered rate in the USA. The residues were <0.01-0.44 mg/kg in whole fruit, <0.01-1.15 mg/kg in peel, and <0.01-0.05 mg/kg in pulp. Residues from trials according to GAP were <0.02 mg/kg in whole fruit in Australia and <0.05 mg/kg in pulp and peel in South Africa.

Limes. Limited data from US trials were provided. Again, excessive rates were used (Table 79).

Table 79. Residues from supervised trials on limes in Florida, USA.

	Application			PHI,	Residues,	Reference
	Form.	kg ai/ha	No.	days	mg/kg	
1972 (Tahiti)	15 GR	33.6	1	147	<0.01	Chemagro 1972d 33087 [1]
1972 (Tahiti)	360 SC	33.6	1	147	<0.01	Chemagro 1972e 33088 [2]
GAP for citrus fruit	**350 EC**	**1.6-8.2**	**1**	**30**		

[1] Single application by broadcast (within dripline). Chromatograms provided.
[2] Single application by soil drench (within dripline). Chromatograms provided.

Oranges. Supervised trials were conducted in Australia, South Africa and the USA. All data were provided in summary form and relevant field details are given as footnotes to Table 80. Recoveries from whole fruit, pulp, peel, leaves, oil and molasses at fortification levels of 0.02-1 mg/kg were reported in Table 61.

Table 80. Residues from trials on oranges in Australia, South Africa and the USA.

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
USA (California), 1970,	10 GR	22.4	1	366	peel	<0.01, 0.02	Chemagro 1970a
(Navel)					pulp	<0.01, <0.01	27442 [1]
USA (California), 1972, (Navel)	15 GR	33.6	1	182	fruit	<0.01	Chemagro 1972f 33148 [2]
USA (Arizona), 1972, (Navel)	360 SC	33.6	1	184	fruit	<0.01	Chemagro 1972g 33077 [3]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
USA (California), 1972, (Navel)	360 SC	33.6	1	182	peel pulp	<0.01 <0.01	33080 [3]
USA (Florida), 1986, (Valencia)	15 GR	22.4	1	31 60 119 181 213 242 273 304 364 31 60 119 181 213 242 273 304 364 31 60 119 181 213 242 273 304 364	pulp peel whole fruit 	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 0.03 0.07 <0.01 0.04 0.01 0.03 0.02 <0.01 <0.01 0.02 <0.01 0.01 <0.01 <0.01 <0.01 <0.01	Mobay 1986d 91352 [4]
USA (Texas), 1986, (Hamlin)	15GR	22.4	1	30 63 123 189 219 252 272 305 378 30 63 123 189 219 252 272 305 378 30 63 123 189 219 252 272 305 378	pulp peel whole fruit 	 0.02 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01 0.71 0.03 0.06 0.07 0.03 <0.01 <0.01 <0.01 <0.01 0.17 <0.01 0.01 0.02 0.01 <0.01 <0.01 <0.01	91354 [5]
USA (California), 1986, (Valencia)	15 GR	22.4	1	21 62 112 151 232 300 332	pulp	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01 <0.01	91356 [6]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
				21	peel	0.01	
				62		<0.01	
				112		0.02	
				151		0.01	
				232		0.02	
				300		0.13	
				332		0.01	
				21	whole fruit	<0.01	
				62		<0.01	
				112		<0.01	
				151		<0.01	
				232		<0.01	
				300		0.03	
				332		<0.01	
USA (Florida), 1986, (Valencia)	360 SC	22.4	1	31	pulp	<0.01	Mobay 1986e 91351 [7]
				60		<0.01	
				119		<0.01	
				180		<0.01	
				212		<0.01	
				241		<0.01	
				273		<0.01	
				304		<0.01	
				364		<0.01	
				31	peel	<0.01	
				60		<0.01	
				119		0.02	
				180		0.02	
				212		0.03	
				241		0.02	
				273		0.02	
				304		0.02	
				364		0.01	
				31	whole fruit	<0.01	
				60		<0.01	
				119		<0.01	
				180		<0.01	
				212		<0.01	
				241		<0.01	
				273		<0.01	
				304		<0.01	
				364		<0.01	
USA (Texas), 1986, (Valencia)	360 SC	22.4	1	30	pulp	<0.01	91353 [8]
				63		0.02	
				123		<0.01	
				189		<0.01	
				219		<0.01	
				252		<0.01	
				272		<0.01	
				305		<0.01	
				378		<0.01	
				30	peel	0.10	
				63		0.38	
				123		0.02	
				189		0.04	
				219		0.03	
				252		0.01	
				272		<0.01	
				305		<0.01	
				378		<0.01	
				30	whole fruit	0.02	
				63		0.09	
				123		<0.01	
				189		<0.01	

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
				219		<0.01	
				252		<0.01	
				272		<0.01	
				305		<0.01	
				378		<0.01	
USA (California), 1986, (Valencia)	360 SC	22.4	1	20	pulp	<0.01	91355 [9]
				62		<0.01	
				112		0.01	
				151		<0.01	
				232		<0.01	
				300		<0.01	
				20	peel	0.01	
				62		<0.01	
				112		0.06	
				151		0.05	
				232		0.06	
				300		0.02	
				20	whole fruit	<0.01	
				62		<0.01	
				112		0.02	
				151		0.01	
				232		0.02	
				300		<0.01	
South Africa (Letsitele), 1976	10 GR	5 g ai/m^2	1	123	fruit	0.08, <u>0.08</u>	S. Afr. Bur. Stds. 1976 0311/8947/N333[10]
				188		0.07, 0.08	
			2	75		<0.02, <0.02	
				123		0.02, <u>0.03</u>	
				188		0.03, 0.03	
Australia 1980, (Navel)	436 g/l	40	1	8	fruit	<u><0.02</u>	Bayer Australia 1980b
							20/80 [11]
GAP							
Australia	**400 liq.**	**30**	**1**	**NS**			
South Africa	**10 GR**	**12 (4 g ai/m^2)**		**150**			
	400 EC	**12 (4 g ai/m^2)**					
USA (for citrus fruit)	**350 EC**	**1.6-8.2**	**1-2**	**30**			

[1] Single application by soil broadcast.
[2] Single application by broadcast (within dripline).
[3] Single application by soil drench (within dripline).
[4] Limit of detection = 0.02 mg/kg, recovery at 2 and 10 mg/kg = 89 and 91% respectively 92 days between 1st and 2nd applications.
[5] Limit of detection = 0.02 mg/kg.
[6] Single application by broadcast and incorporation into soil at immature to maturing fruit stage; plot size 74.3 m^2, sandy soil pH 5.5-6.4, <1% C. Limit of detection = 0.01 mg/kg.
[7] Single application at dormant or blooming or 2.5 or 5 cm diameter fruit; plot size 60 m^2, sandy loam pH 6.5-7.5, 1-2% C. Limit of detection = 0.01 mg/kg.
[8] Single broadcast application and incorporation into soil at mature fruit stage; plot size 0.07 ha, loamy sand soil pH >7.5, <1% C. Limit of detection = 0.01 mg/kg.
[9] Single application by broadcast with incorporation into soil at immature fruit to mature fruit stages; sandy soil, plot size = 74.3 m^2, pH 5.5 6.5, <1% C. Limit of detection = 0.01 mg/kg.
[10] Single application by broadcast and incorporation into soil at dormant or blooming or 2.5 or 5 cm diameter fruit; plot size 60 m^2, sandy loam pH 6.5-7.5, 1-2% C. Limit of detection = 0.01 mg/kg.
[11] Single application at mature fruit stage by broadcast and incorporation into soil; plot size 0.07 ha, loamy sand pH >7.5, <1% C. Limit of detection = 0.01 mg/kg.

The Australian and South African trials were according to GAP, and the residues were <0.02-0.08 mg/kg in the whole fruit. The US trials were at 2.6 or 4 times the maximum registered rate. The residues were <0.01-0.17 mg/kg in whole fruit, <0.01-0.02 mg/kg in pulp and <0.01-0.71 mg/kg in peel.

Apples. Numerous trials were conducted in the USA. All data were in summary form and the available details are included in footnotes to Table 81. Application timings ranged from pre-bloom to green fruit stages. Recoveries determined at fortification levels of 0.05 and 0.1 mg/kg are shown in Table 61.

Table 81. Residues in apples from trials in the USA.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
Washington, 1978, (Winesap)	15 GR	22.4	1	114	pulp peel whole fruit	≤0.01 <0.01 ≤0.01	Mobay, 1978a 65520 [1]
Michigan, 1978, (Golden Delicious)	15 GR	22.4	1	120 130 120 130 120 130	pulp peel whole fruit 	≤0.01 <0.01 <0.01 <0.01 ≤0.01 <0.01	66064 [2]
Virginia, 1978, (Rome Beauty)	15 GR	22.4	1	119 141 119 141 119 141	peel pulp whole fruit 	<0.01 <0.01 ≤0.01 <0.01 ≤0.01 <0.01	66074 [2]
California, 1978, (Winesap)	360 SC	22.4	1	114 114 114	peel pulp whole fruit	<0.01 ≤0.01 ≤0.01	Mobay, 1978b 65619 [1]
New York, 1978, (Ida Red)	360 SC	22.4	1	121 151 121 151 121 151	peel pulp whole fruit 	<0.01 <0.01 ≤0.01 <0.01 ≤0.01 <0.01	66065 [3]
Pennsylvania, 1978, (Golden Delicious)	360 SC	22.4	1	120 130 120 130 120 130	peel pulp whole fruit 	<0.01 <0.01 ≤0.01 <0.01 ≤0.01 <0.01	66075 [4]
Virginia, 1978, (Rome Beauty)	360 SC	22.4	1	119 141 119 141 119 141	peel pulp whole fruit 	<0.01 <0.01 ≤0.01 <0.01 ≤0.01 <0.01	66092 [4]
New York, 1982, (Lodi)	15 GR	22.4	1	102	whole fruit	≤0.01	Mobay 1982a 80769 [5]
Pennsylvania, 1982, (Lodi)	15 GR	22.4	1	79	whole fruit	≤0.01	80770 [5]
West Virginia, 1982, (Rambo)	15 GR	22.4	1	98	whole fruit	≤0.01	80771 [5]
Virginia, 1982, (Yellow Transparent)	15 GR	22.4	1	72	whole fruit	≤0.01	80772 [5]
California, 1982, (Golden Delicious)	15 GR	22.4	1	143	whole fruit	≤0.01	80773 [6]
Washington, 1982, (Gravenstein)	15 GR	22.4	1	125	whole fruit	≤0.01	80774 [7]
Michigan, 1982, (Jersey Mac)	15 GR	22.4	1	107	whole fruit	≤0.01	80775 [6]
New York, 1982, (McIntosh)	15 GR	22.4	1	162	whole fruit	≤0.01	80776 [8]
West Virginia, 1982, (Rome Beauty)	15 GR	22.4	1	176	whole fruit	≤0.01	80777 [9]
Virginia, 1982, (Golden Delicious)	15 GR	22.4	1	155	whole fruit	≤0.01	80778 [10]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference.
	Form.	kg ai/ha	No.	days		mg/kg	
California, 1982, (Red Delicious)	15 GR	22.4	1	143	whole fruit	<0.01	80779 [11]
Washington, 1982, (Golden Delicious)	15 GR	22.4	1	167	whole fruit	<0.01	80780 [7]
Michigan, 1982, (Jonathan)	15 GR	22.4	1	154	whole fruit	<0.01	80781 [6]
New York, 1982, (Lodi)	360 SC	22.4	1	102	whole fruit	<0.01	Mobay, 1982b 80756 [12]
Pennsylvania, 1982, (Lodi)	360 SC	22.4	1	79	whole fruit	<0.01	80757 [10]
West Virginia, 1982, (Rambo)	360 SC	22.4	1	98	whole fruit	<0.01	80758 [9]
Virginia, 1982, (Yellow Transparent)	360 SC	22.4	1	72	whole fruit	<0.01	80759 [10]
California, 1982, (Golden Delicious)	360 SC	22.4	1	143	whole fruit	<0.01	80760 [6]
Washington, 1982, (Gravenstein)	360 SC	22.4	1	125	whole fruit	<0.01	80761 [7]
Michigan, 1982, (Jersey Mac)	360 SC	22.4	1	107	whole fruit	<0.01	80762 [13]
New York, 1982, (McIntosh)	360 SC	22.4	1	162	whole fruit	<0.01	80763 [8]
West Virginia, 1982, (Rome Beauty)	360 SC	22.4	1	176	whole fruit	<0.01	80764 [9]
Virginia, 1982,	360 SC	22.4	1	155	whole fruit	<0.01	80765 [10]
(Golden Delicious)							
California, 1982, (Red Delicious)	360 SC	22.4	1	143	whole fruit	<0.01	80766 [6]
Washington, 1982, (Golden Delicious)	360 SC	22.4	1	167	whole fruit	<0.01	80767 [7]
Michigan, 1982, (Jonathan)	360 SC	22.4	1	154	whole fruit	<0.01	80768 [13]
GAP USA	**350 EC**	**5.4-8.2**		**72**			

[1] Single application by soil broadcast and incorporation at 3.8-5 cm diameter fruit. No chromatograms.
[2] Single application by soil broadcast at green fruit stage. No chromatograms.
[3] Single application by soil broadcast (within dripline) at pink fruit stage. No chromatograms.
[4] Single application by soil broadcast and incorporation (within dripline) at green fruit stage. No chromatograms.
[5] Single application by soil broadcast at pre-bloom stage.
[6] Single application by broadcast at pink bud stage, plot size 20 m^2.
[7] Single application by broadcast at pink bud stage, plot size 30 m^2.
[8] Single application by broadcast at pre-bloom stage; plot size 38.6 m^2.
[9] Single application by broadcast at pre-bloom stage; plot size 58 m^2.
[10] Single application by broadcast at pre-bloom stage; plot size 37m^2.
[11] Single application by broadcast at pink bud stage; plot size 21 m^2.
[12] Single application by broadcast at pre-bloom stage; plot size 12.5 m^2.
[13] Single application by broadcast at pink bud stage; plot size 52 m^2.

The application rates were 2.6 times the maximum registered rate in the USA, but residues in the whole fruit, pulp and peel were below the limit of detection in all the trials. Samples were collected at normal harvest times, so all are considered to be within the GAP PHI.

Cherries. Results of trials in the USA are shown in Table 82. In most cases, single applications were made at flowering or at the immature fruit stages of growth and samples were taken at intervals ranging from 31 to 98 days after application. Fenamiphos residues were <0.01 to 0.18 mg/kg. Recoveries from cherries were determined at fortification levels of 0.01-0.1 mg/kg and are shown in Table 61. Application rates were 2.6 times the maximum rate specified on registered US labels in all but three of the trials, where they were 1.7 times the maximum.

Table 82. Residues in cherries from trials in the USA.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Michigan, 1978, (Montmorency)	15 GR	22.4	1	31	fruit	0.05	Mobay 1978c 66072 [1]
Michigan, 1978, (Montmorency)	360 SC	22.4	1	31	fruit	0.01	Mobay 1978d 66418 [1]
California, 1982, (Pollinator)	15 GR	22.4	1	45	fruit	<0.01	Mobay 1982c 80424 [2]
California, 1982, (Bing)	15 GR	22.4	1	52	fruit	0.03	80425 [2]
Washington, 1982, (Chinook)	15 GR	22.4	1	82	fruit	<0.01	80426 [3]
Oregon, 1982, (Chinook)	15 GR	22.4	1	76	fruit	<0.01	80427 [4]
Michigan, 1982, (Napoleon)	15 GR	22.4	1	52	fruit	0.14, 0.18	80428 [5]
Washington, 1982, (Bing)	15 GR	22.4	1	89	fruit	<0.01	80429 [3]
Oregon, 1982, (Bing)	15 GR	22.4	1	83	fruit	<0.01	80430 [6]
Washington, 1982, (Rainier)	15 GR	22.4	1	98	fruit	<0.01	80431 [3]
California, 1982, (Early Pollinators)	360 SC	22.4	1	52	fruit	0.04, 0.04	Mobay 1982d 80415 [2]
California, 1982, (Bing)	360 SC	22.4	1	52	fruit	0.02	80416 [2]
Washington, 1982, (Chinook)	360 SC	8 + 14.3	2	75	fruit	<0.01	80417 [7]
Oregon, 1982, (Chinook)	360 SC	22.4	1	76	fruit	<0.01	80418 [4]
Michigan, 1982, (Napoleon)	360 SC	22.4	1	52	fruit	0.02, <0.01	80419 [5]
Washington, 1982, (Bing)	360 SC	8 + 14.3	2	82	fruit	<0.01	80420 [7]
Oregon, 1982, (Bing)	360 SC	22.4	1	83	fruit	<0.01	80421 [6]
Washington, 1982, (Rainier)	360 SC	8 + 14.3	2	91	fruit	<0.01	80422 [8]
Michigan, 1982, (Sweet Giant)	360 SC	22.4	1	66	fruit	0.01, 0.02	80423 [5]
GAP USA	**350 EC**	**5.4-8.2**		**45**			

[1] Single application by soil broadcast (within dripline) at green fruit, pit hardening stage. Plot size one tree. No chromatogram.
[2] Single application by soil broadcast at mid-bloom; plot size one tree.
[3] Single application by soil broadcast at bud appearance. Plot size one tree.
[4] Single application by soil broadcast at 85% buds in white bud stage; plot size one tree.
[5] Single application by soil broadcast at early bloom stage; plot size one tree.
[6] Single application by soil broadcast at 95% buds in white bud stage; plot size one tree.
[7] Two applications at 7 days interval by soil broadcast at early bloom and full bloom. Plot size one tree.
[8] Two applications at 7 days interval by soil broadcast at 50% early bloom and 50% full bloom. Plot size one tree.

Peaches. The results of trials carried out in the USA and Italy are shown in Table 83. In most trials, a single application was made at growth stages ranging from pre-flowering to immature fruit and sampling was at intervals from 40 to 150 days after treatment. The residues in most of the trials were below the limit of detection or determination. Recoveries with fortification at 0.05 and 0.1 mg/kg are shown in Table 61.

Table 83. Residues in peaches from trials in the USA and Italy.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
USA (Pennsylvania), 1978, (Red Skin)	15 GR	22.4	1	45 60 90	fruit	0.02 <0.01 <0.01	Mobay 1978e 66047 [1]
USA (New Jersey), 1978, (NJ 232)	15 GR	22.4	1	40 55 85	fruit	0.02 0.02 <0.01	66048 [2]
USA (Pennsylvania), 1978, (Red Skin)	360 SC	22.4	1	45 60 90	fruit	0.02 <0.01 <0.01	Mobay 1978f 66049 [1]
USA (New Jersey), 1978, (NJ 232)	360 SC	22.4	1	40 55 85	fruit	0.01 0.02 <0.01	66050 [2]
USA (Georgia), 1979, (Elberta)	15 GR	22.4	1	45 60	fruit	0.01 0.09	Mobay 1979a 67933 [3]
USA (Sth Carolina), 1979, (Sunlight)	15 GR	22.4	1	73 131	fruit	0.16 <0.01	67934 [4]
USA (New Jersey), 1982, (Garnet Beauty)	15 GR	22.4	1	93	fruit	<0.01	Mobay 1982e 80791 [5]
USA (California), 1982, (Corona)	15 GR	22.4	1	118	fruit	<0.01	80792 [6]
USA (California), 1982, (Starns)	15 GR	22.4	1	130	fruit	<0.01	80793 [6]
USA (California), 1982, (Condor)	15 GR	22.4	1	91	fruit	0.04, 0.05	80794 [5]
USA (Sth Carolina), 1982, (Condor)	15 GR	22.4	1	83	fruit	<0.01	80795 [7]
USA (Michigan), 1982, (Sweet Haven)	15 GR	22.4	1	93	fruit	<0.01	80796 [8]
USA (Georgia), 1982, (Winblo)	15 GR	22.4	1	106	fruit	0.02, 0.01	80797 [4]
USA (Sth Carolina), 1982, (Rio-Oso-Gem)	15 GR	22.4	1	150	fruit	<0.01	80798 [7]
USA (Sth Carolina), 1982, (Condor)	15 GR	22.4	1	83	fruit	0.10, 0.13, 0.11	80802 [7]
USA (Sth Carolina), 1982, (Red Globe)	15 GR	22.4	1	122	fruit	0.01	80803 [7]
USA (Sth Carolina), 1982, (Rio-Oso-Gem)	15 GR	22.4	1	150	fruit	<0.01	80804 [7]
USA (New Jersey), 1982, (Garnet Beauty)	360 SC	22.4	1	93	fruit	<0.01	Mobay 1982f 80782 [5]
USA (California), 1982, (Corona)	360 SC	22.4	1	118	fruit	<0.01	80783 [6]
USA (California), 1982, (Starns)	360 SC	22.4	1	130	fruit	<0.01	80784 [6]
USA (California), 1982, (Condor)	360 SC	22.4	1	91	fruit	0.01	80785 [5]
USA (Sth Carolina), 1982, (Condor)	360 SC	22.4	1	83	fruit	<0.01	80786 [7]
USA (Michigan), 1982, (Sweet Haven)	360 SC	22.4	1	93	fruit	<0.01	80787 [8]
USA (Sth Carolina), 1982, (Red Globe)	360 SC	22.4	1	122	fruit	<0.01	80788 [7]
USA (Georgia), 1982, (Winblo)	360 SC	22.4	1	106	fruit	<0.01	80789 [9]
USA (Sth Carolina), 1982, (Rio-Oso-Gem)	360 SC	22.4	1	150	fruit	<0.01	80790 [7]
USA (Sth Carolina), 1982, (Condor)	360 SC	22.4	1	83	fruit	<0.01	80799 [7]
USA (Sth Carolina), 1982, (Red Globe)	360 SC	22.4	1	122	fruit	0.08, 0.08	80800 [7]
USA (Sth Carolina), 1982, (Rio-Oso-Gem)	360 SC	22.4	1	150	fruit	<0.01	80801 [7]

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Italy (Bagnacavallo), 1986 (May Grand)	5 GR	25	1	85 93	fruit (depitted)	<0.02, <0.02 <0.02, <0.02	Bayer 1986c 5238-86 [10]
GAP **USA** **Italy**	 **350 EC** **5 GR**	 **5.4-8.2** **10-15**	 **1**	 **45** **120**			

[1] Single application to bare ground by broadcast with incorporation; growth stage at application: green fruit. Plot size two trees. No chromatograms provided.
[2] Single application by broadcast (within dripline); plot size 37.3 m^2. No chromatograms provided.
[3] Single application by broadcast (within dripline); growth stage at application: bloom.
[4] Single broadcast application (within dripline) at pre-bloom stage.
[5] Single broadcast application (within dripline) at pre-bloom stage; plot size 3 trees.
[6] Single application by broadcast and incorporation; plot size one tree; growth stage at application: late post-bloom.
[7] Single application by broadcast and incorporation at full bloom stage; plot size 9 trees.
[8] Single application by broadcast at pink stage; plot size 1 tree.
[8] Single application by soil broadcast at pre-bloom stage; plot size 58 m^2.
[9] Single application by spreading by hand at sepal fall; plot size 100 m^2, clay loam soil, pH 7.5, 2% C. Limit of determination 0.02 mg/kg, recovery at 0.02 mg/kg 87%. No chromatograms.

The rates in the US trials were 2.7 times the maximum registered rate. Residues in whole fruit were <0.01 to 0.16 mg/kg at the earliest pre-harvest intervals. In the Italian trial the application was at 1.7 times the GAP rate.

Grapes. Supervised trials were conducted in the USA, Mexico, South Africa and Chile. Residues were determined in grapes and raisins in some of the US trials. Recoveries from grapes, raisins and raisin trash with fortification at 0.01-0.1 mg/kg are shown in Table 61.

Table 84. Residues in grapes from supervised trials in Chile, Mexico, South Africa and the USA.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Mexico, (Valle de Mexicali), 1979, (Thompson Seedless)	15 GR	4.48	1	97	fruit	0.01	Mobay 1979b 68227 [1]
Mexico, (Sonora), 1979, (Thompson Seedless)	15 GR	4.48	1	69	fruit	0.02	68231 [2]
Mexico (Sonora), 1979, (Thompson Seedless)	15 GR	6.72	1	69	fruit	0.03	68232 [2]
Mexico (Sonora), 1979, (Thompson Seedless)	15 GR	4.48	1	70	fruit	0.02	68234 [3]
USA (California), 1981, (Ruby Cabernet)	15 GR	6.72	3	58 72 85	fruit	0.03 0.02 0.02	Mobay 1981c 69658 [4]
USA (California), 1981, (Zinfandel)	15 GR	6.72	3	56	fruit	0.01	80069 [5]
USA (California), 1981, (Chenin blanc)	15 GR	6.72	3	58	fruit	0.09, 0.04	80070 [4]
USA (Oregon), 1981, (White Riesling)	15 GR	6.72	3 3	56 70	fruit fruit	0.02 0.01	80071 [6]
USA (California), 1981, (Ruby Cabernet)	15 GR	6.72	3	55 70	fruit	<0.01 <0.01	80197 [7]
USA California), 1981, (Chenin blanc)	15 GR	6.72	3	50 63	fruit	0.07 <0.01	80204 [8]
USA (California), 1981, (Ruby Cabernet)	360 SC	6.72	3 3 3	58 72 85	fruit fruit fruit	<0.01 <0.01 <0.01	Mobay 1981d 69659 [9]
USA (California), 1981, (Thompson Seedless)	360 SC	6.72	3	55 70	fruit fruit	0.07 0.05	69745 [10]
				80	fruit	0.04	
USA (California), 1981,	360 SC	6.72	3	56	fruit	<0.01	80075 [11]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
(Tokay)							
USA (California), 1981, (Chenin Blanc)	360 SC	6.72	3	58 72 85	fruit fruit fruit	0.02 <0.01 <0.01	80076 [12]
USA (California), 1981, (White Riesling)	360 SC	6.72	3	56 70 84	fruit fruit fruit	0.03 <0.01 <0.01	80077 [13]
USA (California), 1981, (Thompson Seedless)	360 SC	6.72	3	56 73	fruit raisins fruit raisins	0.02 0.03 0.01 0.01	80080 [14]
USA (California), 1981, (Zinfandel)	360 SC	6.72	3	46 60 74	fruit	<0.01 <0.01 <0.01	80199 [15]
USA (California), 1981, (Emperor)	360 SC	6.72	3	55 70	fruit	<0.01 <0.01	80200 [16]
USA (California), 1981, (Chenin Blanc)	360 SC	6.72	3	0 13	fruit	0.01 <0.01	80206 [17]
USA (California), 1981, (Thompson Seedless)	360 SC	10	2	0 1 3 7	fruit	<0.01 <0.01 <0.01 <0.01	80081 [18]
USA, (California), 1981, (Emperor)	360 SC	10	2	0 7	fruit	0.01 0.01	80082 [19]
				14		0.03	
USA (California), 1981, (Thompson Seedless)	15 GR	10	2	0 1 3 7 14 21	fruit	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	80083 [20]
USA (California), 1981, (Emperor)	15 GR	10	2	0 1 3 7 14 21	fruit	0.03 0.02 <0.01 0.03 0.02 0.03	80084 [21]
USA (California), 1981, (Emperor)	360 SC	10	2	0 1 3 7 14	fruit	<0.01 <0.01 <0.01 <0.01 <0.01	80207 [22]
USA (California), 1981, (Emperor)	15 GR	10	2	0 1 3 7 14	fruit	0.02 <0.01 0.02 0.02 0.02	80208 [22]
South Africa, 1982, (Clairette Blanche)	400 EC 400 EC	10 20 10 10 20	1 1 2 1 1	178 178 178 177 177	fruit fruit fruit fruit fruit	<0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05	S. Afr. Bur. Stds. 1983 311/88476/W331 [23]
South Africa (Paarl), 1987, (Queen of the vineyard) (Alphonse Lavalee)	400 EC 400 EC	1 g ai/m^2 2 g ai/m^2 1 g ai/m^2	1 1 1	97 117 129 97 117 129 97 117 129	fruit fruit fruit	<0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05,<0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05 <0.05, <0.05	S. Afr. Bur. Stds. 1987 311/88097/D34 [24]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
		2 g ai/m^2	1	97 117 129	fruit	<0.05, <0.05 <0.05, <0.05 <0.05, <0.05	
Chile (Cuarta), 1988, (Thompson Seedless)	400 EC	6	1	73	fruit	<0.01, 0.01	Fundacion Chile 1988 CHL-RENE0187-A1 [25]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	12	1	73	fruit	0.02, 0.02	CHL-RENE0187-A2 [25]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	6	1	80	fruit	≤0.01, <0.01	CHL-RENE0187-A3 [25]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	12	1	80	fruit	0.02, 0.02	CHL-RENE0187-A4 [25]
Chile (Metropolitana), 1987, (Thompson Seedless)	400 EC	12	1	117	fruit	<0.01, <0.01	CHL-RENE0187-B1 [26]
Chile (Meteropolitana), 1987, (Thompson Seedless)	400 EC	24	1	117	fruit	<0.01, <0.01	CHL-RENE0187-B2 [26]
Chile (Metropolitana), 1987, (Thompson Seedless)	400 EC	12	1	125	fruit	<0.01, <0.01	CHL-RENE0187-B3 [26]
Chile (Metropolitana), 1987, (Thompson Seedless)	400 EC	24	1	125	fruit	<0.01, <0.01	CHL-RENE0187-B4 [26]
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	12	1	103	fruit	<0.01, <0.01	CHL-RENE0187-C1 [27]
Chile (Quinta), 1987,	400 EC	24	1	103	fruit	<0.01, <0.01	CHL-RENE0187-C2 [27]
(Thompson Seedless)							
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	12	1	110	fruit	<0.01, <0.01	CHL-RENE0187-C3 [27]
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	24	1	110	fruit	<0.01, <0.01	CHL-RENE0187-C4 [27]
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	24	2	110	fruit	<0.01, <0.01	CHL-RENE0287-A1 [28]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	5.16	2	84	fruit	<0.01, 0.01	CHL-RENE0287-A2 [29]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	10.32	2	84	fruit	0.02, 0.02	CHL-RENE0287-A3 [29]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	5.16	2	90	fruit	≤0.01, <0.01	CHL-RENE0287-A4 [29]
Chile (Cuarta), 1987, (Thompson Seedless)	400 EC	10.32	2	90	fruit	0.01, 0.01	CHL-RENE0287-C1 [29]
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	12	2	103	fruit	<0.01, <0.01	CHL-RENE0287-C2 [30]
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	24	2	103	fruit	<0.01, <0.01	CHL-RENE0287-C3 [30]
Chile (Quinta), 1987, (Thompson Seedless)	400 EC	12	2	110	fruit	<0.01, <0.01	CHL-RENE0287-C4 [30]
GAP **Chile** **Mexico** **South Africa** **USA**	**400 EC** **400 EC** **10 GR** **360 EC**	**6-8** **2.8-4.8** **4-6** **1**g ai/m^2 **3.3-6.54 (band)**	 **1** **1-4**	**45** **45** **100** **2**			

[1] Single application as double sidedress band shortly before flowering; plot size 19.5 m^2, 0.3 m row spacing.
[2] Single application as double sidedress band at flowering; plot size 802 m^2, 0.3 m row spacing.
[3] Single application as double sidedress band at flowering; plot size 535 m^2, 0.3 m row spacing.
[4] Three applications (20 and 13 day intervals) by soil broadcast at blooming stage; plot size 89.1 m^2, 0.3 m row spacing.
[5] Three applications (41 and 51 day intervals) by soil broadcast at 0.5 m high plants, pre-bloom and post-bloom stages; plot size 60.1 m^2, 0.22 m row spacing.

[6] Three applications (35 and 39, 34 and 42 day intervals) by soil broadcast and incorporation at full bloom, 0.16-0.6 cm and 1.2 cm diameter fruit; bud stage, post-bloom and 0.9-1.2 cm diameter fruit; plot size 8.9 m^2.
[7] Three applications (39 and 37 day intervals) by soil broadcast and incorporation at 0.15 m growth, bloom and berry formation; plot size 89.2 m^2, 0.3 m row spacing.
[8] Three applications (12 and 23 day intervals) by soil broadcast and incorporation at bud break, bloom and berry formation; plot size 89.2 m^2, 0.3 m row spacing.
[9] Three applications (29 and 13 day intervals) by soil broadcast and incorporation at blooming stage; plot size 89.2 m^2, 0.3 m row spacing.
[10] Processing study. Three applications (14 and 13 day intervals) by soil incorporation at blooming stage; plot size 89.1 m^2, row spacing 3 m.
[11] Three applications (31 and 50 day intervals) by soil broadcast at 0.15 m growth, pre-bloom and post-bloom stages; plot size 45.1 m^2, row spacing 0.23 m. Chromatograms provided in full report.
[12] Three applications (23 and 13 day intervals) by soil broadcast at blooming stage, plot size 89.2 m^2, row spacing 0.3 m.
[13] Three applications (35 and 39, 34 and 42, 19 and 52 day intervals) by soil broadcast and incorporation at full bloom, 0.16-0.6 cm and 1.2 cm diameter fruit; bud stage, post-bloom and 0.9-1.2 cm diameter fruit; plot size 8.9 m^2.
[14] Processing study. Three applications (49 and 36 days intervals) by soil broadcast spray at 5-10 cm shoots, blooming and post-bloom; plot size 38.9 m^2, row spacing 0.3 m. Chromatograms provided in full report.
[15] Three applications (31 and 62 day intervals) by soil broadcast spray at 0.15 m growth, pre-bloom and post-bloom stages; plot size 60.1 m^2; row spacing 0.23 m.
[16] Three applications (39 and 37 day intervals) at 0.15 m growth, bloom and berry formation; plot size 0.3 m, row spacing 0.3 m.
[17] Three applications (57 and 73 days intervals) by soil broadcast spray and incorporation at bud break, bloom and berry formation stages; plot size 89.1 m^2, row spacing 0.3 m.
[18] Two applications at 29 day interval by broadcast soil spray at fruiting and mature fruit stages; plot size 23 m^2, 0.2 m row spacing.
[19] Two applications at 42 days interval by soil broadcast spray at maturing fruit stages; plot size 78 m^2, 0.3 m row spacing.
[20] Two applications by soil broadcast with incorporation at 29 days interval at fruiting and mature fruit stages; plot size 23.4 m^2, 0.2 m row spacing.
[21] Two applications at 42 days interval by soil broadcast and incorporation at maturing fruit stages; plot size 78 m^2, 0.3 m row spacing.
[22] Two applications by soil broadcast spray and incorporation at 36 days interval at 'colour changeng' and maturing fruit stages; plot size 78 m^2, 0.3 m row spacing.
[23] Applications to vines by knapsack. Recovery at 0.1 mg/kg of F, FSO, FSO_2 = 95%, 91% and 92% respectively. Limit of detection = 0.05 mg/kg.
[24] Limit of detection = 0.05 mg/kg, recovery of F, FSO and FSO_2 at 0.1 mg/kg = 106, 86; 90, 74; 110, 87% respectively. Samples stored for 158 days before analysis.
[25] Single application by drip irrigation 10 days after end of flowering; plot size 768 m^2. Soil type 'Franco arcillosa', 1% C. Limit of detection = 0.01 mg/kg, recovery at 0.2 mg/kg = 93.6%, at 0.04 mg/kg = 84.3%.
[26] Single application by drip irrigation at plant growth 50 to 70 cm; plot size 896 m^2, soil type 'Franca', pH 6.5-7.5, 1.58-2.11% C. Limit of detection = 0.01 mg/kg, recovery at 0.2 mg/kg = 93.6%, at 0.04 mg/kg = 84.3%.
[27] Single application by drip irrigation at pre-flowering stage; plot size 551 m^2, soil type 'Franco arcillosa', pH 7.5 0.63% C. Limit of detection = 0.01 mg/kg, recovery at 0.2 mg/kg = 93.6%, at 0.04 mg/kg = 84.3%.
[28] Two applications by drip irrigation at pre-flowering stages (231 day interval); plot size 551 m^2, soil type 'Franco arcillosa', pH 7.5 0.63% C. Limit of detection = 0.01 mg/kg, recovery at 0.2 mg/kg = 93.6%, at 0.04 mg/kg = 84.3%.
[29] Two applications by drip irrigation at pre-flowering and flowering (158 day interval); plot size 1287 m^2, soil type 'Franco arcillosa', pH 7.8, 1.58% C. Limit of detection = 0.01 mg/kg, recovery at 0.2 mg/kg = 93.6%, at 0.04 mg/kg = 84.3%.
[30] Two applications by drip irrigation at pre-flowering and flowering stages (231 day interval); plot size 551 m^2, soil type 'Franco arcillosa', pH 7.5, 0.63% C. Limit of detection = 0.01 mg/kg, recovery at 0.2 mg/kg = 93.6%, at 0.04 mg/kg = 84.3%.

The US and Chilean trials were at rates in excess of the registered use patterns. The residues in fruit from trials considered to be according to GAP were <0.01-0.09 mg/kg at harvest.

Bananas. Residues from supervised trials in Australia, Brazil, Costa Rica, Spain and the Windward Islands are shown in Table 85. Most of the data were provided in summary form, with reported recoveries and details shown as footnotes to the Table. In some cases chromatograms were not provided. Where the field and analytical phases of the trial were reported in accordance with GLP requirements the trial is described in detail below. From 1 to 3 sprays were applied per season and the residues were determined in the whole fruit, or pulp and peel separately. Where residues in pulp and peel were reported separately and were below the limit of detection in both, the residues in the whole fruit are assumed to below the limit of detection. Recoveries were reported in supplement E019 to method 00024/M 002 at fortification levels of 0.02-0.5 mg/kg (Specht, 1995). Recoveries of fenamiphos sulfone were 64-97%; other recoveries are shown in endnotes to Table 85.

In a Spanish trial in the Canary Islands (Ohs, 1996), Nemacur 400 EC was applied twice to established banana plants at a rate of 5 g ai/plant by drip irrigation at re-treatment intervals of 161 or 166 days; the first application was at a growth stage of 5 to 9 leaves unrolled and the second was about 90 days before harvest. Plot sizes were 225, 471 and 482 m^2; the cropping density was estimated as 700 plants/ha. Samples of bananas were taken at 14/15, 30/32, 53/55, 68/70 and 90 days after treatment and residues were determined in the whole fruit, pulp and peel.

In a subsequent trial in the Canary Islands (Heinemann and Ohs, 1997g), Nemacur 240 CS was again applied twice at 5 g ai/plant by drip irrigation, but with an interval of 210 or 212 days between treatments. The first application was at 17 or 25 leaves unrolled and the second at the end of flowering, or approximately 89 days before harvest. Crop densities were 1700 or 2000 plants/ha, which corresponded to application rates of 8.6 or 10 kg ai/ha. Samples were taken at 28/31, 60 and 89 days after the final treatment and residues were determined in whole fruit, pulp and peel.

Table 85. Residues in bananas from trials in Australia, Brazil, Costa Rica, Spain (Canary Islands) and the Windward Islands.

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference.
	Form.	kg ai/ha	No	days		mg/kg	
Australia (WA), 1971, (Mons Mari)	400 EC	4.48	1	28	whole fruit	<0.01	Bayer Austrl. 1971I 23/71a [1]
Australia (WA), 1971, (Mons Mari)	400 EC	8.96	1	28	whole fruit	<u><0.01</u>	23/71b [1]
Australia (NSW), 1972, (Williams Hybrid)	5 GR	2.8 g ai/stool	2	21	whole fruit	<u><0.01</u>	Bayer Austrl. 1972 14/72a [2]
Australia (NSW), 1972, (Williams Hybrid)	5 GR	2.8 g ai/stool	2	112	whole fruit	<u><0.01</u>	14/72b [2]
Costa Rica (Limon), 1970, (Giant Cavendish)	10 GR	6 g ai/plant	1	1	pulp	<0.02	Burrows 1971a 30164 [3]
				3		<0.02 (*0.03 c*)	
				7		<0.02	
				14		<0.02	
				30		<0.02	
				61		<0.02	
				90		<u><0.02</u>	
				195		<0.02	
				1	peel	<0.02	
				3		<0.02	
				7		<0.02	
				14		<0.02	
				30		<0.02	
				61		<0.02	
				90		<u>0.03</u>	
				195		<0.02	
		9 g ai/plant	1	1	pulp	<0.02	
				3		<0.02	
				7		<0.02	
				14		<0.02	
				30		<0.02	
				61		<u><0.02</u>	
				90		<0.02	
				195		<0.02	
				1	peel	<0.02	
				3		<0.02	
				7		<0.02	
				14		<0.02	
				30		<0.02	
				61		<u><0.02</u>	
				90		<0.02	
				195		<0.02	
		12 g ai/plant		1	pulp	<0.02	
				3		<0.02	
				7		<0.02	

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference.
	Form.	kg ai/ha	No	days		mg/kg	
				14		<0.02	
				30		<0.02	
				61		<0.02	
				90		<0.02	
				195		<0.02	
				1	peel	<0.02	
				3		<0.02	
				7		<0.02	
				14		<0.02	
				30		<0.02	
				61		<0.02	
				90		<0.02	
				195		<0.02	
Windward Islands, 1970, (Robusta)	10 GR	2.8 g ai/plant	1	1	pulp	<0.025	Burrows, 1971b 30203 [4]
				2		<0.025	
				7		<0.025	
				14		<0.025	
				31		<0.025	
				69		<0.025	
				96		<0.025	
				1	peel	<0.025	
				2		<0.025	
				7		<0.025	
				14		<0.025	
				31		<0.025	
				69		<0.025	
				96		<0.025	
		5.7	1	1	pulp	<0.025	
				2		<0.025	
				7		<0.025	
				14		<0.025	
				31		<0.025	
				69		<0.025	
				96		<0.025	
				1	peel	<0.025	
				2		<0.025	
				7		<0.025	
				14		<0.025	
				31		<0.025	
				69		<0.025	
				96		<0.025	
		11.3	1	1	pulp	<0.025	
				2		<0.025	
				7		<0.025	
				14		<0.025	
				31		<0.025	
				69		<0.025	
				96		<0.025	
				1	peel	<0.025	
				2		<0.025	
				7		<0.025	
				14		<0.025	
				31		<0.025	
				69		<0.025	
				96		<0.025	
Brazil, 1983	10 GR	4 g ai/plant	1	95	whole fruit	<0.1	Fundacao de C. e T.1984 BRA-71133 [5]
Brazil 1983	10 GR	4 g ai/plant	1	32	whole fruit	<0.1	BRA-71134 [5]
Brazil 1983	10 GR	4 g ai/plant	1	62	whole fruit	<0.1	BRA-71135-B[5]
Brazil (Juquia), 1988, (Nanicao)	10 GR	3 g ai/plant	1	30	whole fruit	<0.1	U. Sao Paulo 1988a BRA-MUBP A87-1-A[6]
				45		<0.1	
				60		<0.1	

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference.
	Form.	kg ai/ha	No	days		mg/kg	
Brazil (Juquia), 1988, (Nanicao)	10 GR	6 g ai/plant	3	30	whole fruit	≤0.1	BRA-MUBP A87-1-B[6]
Canary Isl. (Buenavista del Norte), 1994 (Pequena Enana)	400 EC	5 g ai/plant	2	15 30 55 70 90 90 90	whole fruit pulp peel	<0.02 <0.02 <0.02 <0.02 ≤0.02, <0.02 ≤0.02 <0.02	Ohs 1996 40395-94 [7]
Canary Isl. (Valle de Guerra), 1994 (Pequena Enana)	400 EC	5 g ai/plant	2	14 32 53 68 90 90 90	whole fruit pulp peel	<0.02 <0.02 <0.02 <0.02 ≤0.02, <0.02 ≤0.02 <0.02	40396-94 [8]
Canary Isl. (Adeje), 1994, (Pequena Enana)	400 EC	5 g ai/plant	2	90	pulp peel whole fruit	≤0.02 <0.02 ≤0.02, <0.02	40397-94 [9]
Canary Isl. (Adeje), 1996, (Pequena Enana)	240 CS	5 g ai/plant	2	31 60 	green fruit ripe fruit green fruit ripe fruit	<0.02, <0.02 0.02, 0.02 <0.02 <0.02	Heinemann and Ohs 1997g 0274-96 [10]
				89 31 60 89 31 60 89	green fruit ripe fruit pulp peel 	<0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02 <0.02, <0.02 <0.02, <0.02 0.021 <0.02, <0.02	
Canary Isl. (Buenavista del Norte), 1996, (Pequena Enana)	240 CS	5 g ai/plant	2	28 60 89 28 60 89 28 60 89	ripe fruit green fruit green fruit pulp peel 	<0.02, <0.02 <0.02, <0.02 <0.02 <0.02 <0.02, <0.02 <0.02, <0.02 <0.02, <0.02 <0.02 <0.02, <0.02 <0.02, <0.02 <0.02 <0.02, <0.02	0368-96 [11]
GAP							
Australia	**100 G**	**2.5 g ai/plant**	**3**				
	400 liq.	**9.6-12 kg ai/ha**	**3**				
Brazil	**10 GR**	**2-3 g ai/plant**	**2**	**30**			
Costa Rica	**10 GR**	**5 kg ai/ha**	**1**	**60**			
	15 GR	**5.1**	**1**	**60**			
Spain	**10 GR**	**1.5-3 g ai/plant**		**60**			
	400 EC	**10-20 kg ai/ha**		**90**			

[1] Application by flood irrigation; plot size 0.018 ha (20 stools). Limit of detection = 0.01 mg/kg, recovery at 0.1 mg/kg = 73%, at 0.5 mg/kg = 60%. No chromatograms provided.

[2] Two applications by hand in 15 cm band width 231 days apart. Limit of detection 0.01 mg/kg; recovery at 0.1 mg/kg = 94%, at 0.5 mg/kg = 91%.

[3] Single application by broadcast around individual plants 3.5 months before harvest. Limit of detection = 0.02 mg/kg, recovery of F at 0.1 mg/kg = 104, 71 and 63% from pulp and 58, 60 and 59% from peel. Recovery of FSO and FSO_2 at 0.1 mg/kg = 65 and 85% respectively from pulp and 53 and 63% from peel. Recovery of F at 0.5 mg/kg = 90% from pulp and peel.

[4] Single application in a 61 cm band around plant by spreading; heavy clay soil. Limit of detection = 0.025 mg/kg; recovery of FSO from peel at 0.05 mg/kg = 79%, recovery of F and FSO_2 at 0.1 mg/kg = 85 and 90% from pulp and 89 and 85% from

peel. Recovery of FSO = 77% from pulp at 0.4 mg/kg, 85% from peel at 0.1 mg/kg. Recovery of F at 0.4 mg/kg = 70% from peel.
[5] Single application by spreading and incorporation. Limit of determination = 0.1 mg/kg, recovery at 0.1 mg/kg = 80%. No chromatograms provided.
[6] Three applications (189 and 235 day intervals) by spreading; stage at last application fruit development; plot size 70 plants; clay sand, pH 5, 1.3% C. Limit of determination = 0.1 mg/kg, recoveries at 0.1 mg/kg 83-91%.
[7] Two applications by drip irrigation at 166 day interval; plot size 482 m^2, loamy sand soil, pH 8, 1.7% C, age of crop >10 years.
[8] Two applications by drip irrigation at 161 day interval; plot size 471 m^2, clay sand soil, pH 7.1, 1.4% C, age of crop >10 years.
[9] Two applications by irrigation at 161 day interval; plot size 225 m^2, clay sand soil, pH 7.6, 1.3% C, age of crop >10 years. Recoveries at 0.02 mg/kg from fruit 64-91% (n = 4), from pulp 77-94% (n = 4), from peel 70-97% (n = 4).
[10] Two applications by drip irrigation at 212 day interval, first application at 25 leaves unrolled and second at end of flowering; crop density 2000 plants/ha, clay sand soil, pH 7.1-7.6, 1.3-1.8% C.
[11] Two applications by drip irrigation at 17 leaves unrolled and end of flowering with 210 day interval.

Residues in bananas and banana pulp were below the limit of detection or determination in all trials. The trials in Costa Rica were designed to allow for crop densities of 416-833 plants/ha and those in the Windward Islands to allow for crop densities of 412-1785 plants/ha.

Pineapples. Data were predominantly from trials in Hawaii. Some trials from Australia and Puerto Rico were also reported. All the data were in the form of summary sheets, usually with chromatograms attached. Recoveries were reported from pineapple pulp, bran, foliage, forage and crowns, with fortification concentrations of 0.05-0.1 mg/kg in Table 61. Details of applications and timing are shown as footnotes to Table 86. In the Hawaiian trials residues were determined in by-products which could be fed to livestock such as foliage, crowns, stumps and bran, as well as in the edible portion of the commodity.

Table 86. Residues in pineapples and pineapple by-products.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
Hawaii, (Libby), 1970, (Smooth Cayenne)	10 GR 3 LC	22.4 + 11.2 + 11.2 P	1 + 1 + 1	270	whole fruit wet bran foliage soil	<0.01 0.01 <0.01 0.34 (*0.08 c*)	Chemagro 1970b 27703 [1]
Hawaii, (Dole Lani), 1970, (Smooth Cayenne)	10 GR 3 LC	22.4 + 11.2 + 11.2 P	1 + 1+ 1	255	whole fruit wet bran foliage soil	0.03 0.03 8.68 2.17	27704 [2]
Hawaii, (Wahiawa), 1970, (Smooth Cayenne)	10 GR 3 LC	22.4 + 11.2 + 11.2 P	1 + 1+ 1	238	whole fruit wet bran foliage soil	<0.01 <0.01 0.14, 0.11 0.44	27705 [3]
Hawaii, (Wahiawa), 1970, (Smooth Cayenne)	10 GR 3 LC	22.4 + 11.2 + 11.2 P	1 + 1+ 1	262	whole fruit wet bran foliage soil	<0.01 <0.01 <0.01 0.06	27707 [4]
Hawaii, (Wahiawa), 1970, (Smooth Cayenne)	10 GR 3 LC	22.4 + 11.2 + 11.2 P	1 + 1+ 1	265	whole fruit wet bran foliage soil	<0.01 0.03 0.94 0.14	27710 [4]
Hawaii (Wahiawa), 1970, (Smooth Cayenne)	10 GR + 3 LC	22.4+ 11.2 + 11.2 P	1 +1 + 1	251	whole fruit wet bran foliage soil	<0.01 <0.01 <0.01 0.18	27711 [5]
Hawaii (Oahu), 1972, (Cayenne)	15 GR + 3 SC	22.4 + 5.6 P	1 + 4	217 224	whole fruit bran foliage	0.02 0.13 0.05	Chemagro 1972h 32018 [6]
Hawaii (Molokai), 1971	15 GR + 3 SC	22.4 + 5.6 P	1 + 4	192	whole fruit bran	<0.01 <0.01	32019 [7]

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
				199	foliage	0.06	
Hawaii (Molokai), 1973	15 GR + 360 SC	22.4 + 5.6 P	1 + 6	31	pulp bran dry bran foliage	0.14 1.07 2.30 4.78	Chemagro 1973e 39012 [8]
Hawaii (Oahu), 1973	15 GR + 360 SC	22.4 + 5.6 P	1 + 6	83	pulp bran dry bran foliage	0.02 0.11 (*0.02 c*) 0.35 (*0.07 c*) 0.05 (*0.11 c*)	39013 [9]
Australia, 1974, (Smooth Cayenne)	43.6%	1.1	5	330	whole fruit	<0.01	Bayer Australia 1974 2/74a [10]
Australia, 1974, (Smooth Cayenne)	43.6%	2.2	5	330	whole fruit	<0.01	2/74b [10]
Australia, 1974, (Smooth Cayenne)	43.6%	4.5	5	330	whole fruit	<0.01	2/74c [10]
Puerto Rico (Manati), 1974, (Smooth Cayenne)	15 GR + 3 SC	22.4 + 11.2 P	1 + 3	223	pulp bran crowns leaves	<0.01 <0.01 <0.01 <0.01	Chemagro 1975 44744 [11]
Puerto Rico (Manati), 1975, (Smooth Cayenne)	15 GR + 3 SC	22.4 + 5.6 P	1 + 3	223	pulp bran crowns leaves	<0.01 <0.01 <0.01 <0.01	44745 [11]
Hawaii (Maui), 1976, (Smooth Cayenne)	3 SC	5.6 P	6	237	pulp wet bran dry bran crowns leaves stumps	<0.01 <0.01 <0.01 <0.01 <0.01 0.08	Chemagro 1976d 48145 [12]
Hawaii (Maui), 1976, (Smooth Cayenne)	3 SC	2.8 P	6	237	pulp wet bran dry bran crowns leaves stumps	<0.01 <0.01 <0.01 <0.01 <0.01 0.12	48146 [12]
Hawaii (Lanai), 1976, (Smooth Cayenne)	3 SC	5.6 R	8	159	pulp wet bran dry bran crowns leaves stumps	<0.01 <0.01 0.02 <0.01 0.09 0.11	48147 [13]
Hawaii (Maui), 1976, (Smooth Cayenne)	3 SC	5.6 R	4	237	pulp wet bran dry bran crowns leaves stumps	<0.01 <0.01 <0.01 <0.01 <0.01 0.13	48148 [14]
Hawaii (Lanai), 1976, (Smooth Cayenne)	3 SC	5.6 R	4	256	pulp wet bran dry bran crowns leaves stumps	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	48150 [15]
Hawaii (Lanai), 1976, (Smooth Cayenne)	15 GR + 3 SC	22.4+ 5.6 P	1 + 4	256	pulp wet bran dry bran crowns leaves stumps	<0.01 <0.01 <0.01 <0.01 <0.01 <0.01	Chemagro 1976e 48149 [16]

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 EC	22.4 + 2.24 + 3.36 P	1 + 1 + 7	27	foliage pulp bran	0.01 <u>≤0.01</u> <0.01	Mobay 1982g 80646 [17]
Hawaii (Maui), 1982, (Cayenne)	360 SC	22.4 + 3.17 + 3.36 P	1 + 6 + 1	30	foliage pulp bran crown	<0.01 <u>≤0.01</u> <0.01 <0.01	80647 [18]
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 SC	3.36 + 1.12 P	14 + 1	27	foliage pulp bran	0.04 <u>≤0.01</u> <0.01	80648 [19]
Hawaii (Maui), 1982, (Cayenne)	360 SC	11.2 + 3.36 P	1 + 10	30	foliage pulp bran crown	0.03 <u>≤0.01</u> <0.01 <0.01	80649 [20]
Hawaii (Oahu), 1982, (Smooth Cayenne)	360 SC	22.4 + 2.24 + 3.36 P	1 + 1 + 6	36	foliage pulp bran crown	0.06 <u>0.01</u> <0.01 0.03	80650 [21]
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	145	foliage pulp bran crown	0.02 <u>≤0.01</u> <0.01 <0.01	80658 [22]
Hawaii (Oahu), 1982, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	31	foliage pulp bran crown	0.22 <u>≤0.01</u> <0.01 0.02	80659 [23]
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	145	foliage pulp bran crown	0.01 <u>≤0.01</u> <0.01 <0.01	80660 [22]
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	145	foliage pulp bran crown	0.03 <u>≤0.01</u> <0.01 0.02	80661 [22]
Hawaii (Oahu), 1982, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	31	foliage pulp bran crown	0.07 <u>≤0.01</u> <0.01 0.05	80662 [23]
Hawaii (Oahu), 1982, (Smooth Cayenne)	360 SC	2.8 R	8	31	wet bran pulp crown foliage	0.25 <u>0.02</u> 0.30 1.21	82389 [24]
Hawaii (Oahu), 1982, (Smooth Cayenne)	360 SC	3.37 + 4.5 R	4 + 2	32	wet bran pulp dried bran foliage	0.71 <u>0.05</u> 2.60 2.64	82390 [25]
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 SC	3.36 + 1.12 P	14 + 1	27	wet bran pulp crowns foliage	0.10 <u>0.01</u> 0.08 0.17 (*0.03 c*)	82391 [26]
Hawaii (Lanai), 1982, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	139	wet bran pulp crowns foliage	<0.01 <u>≤0.01</u> 2.27 0.05	82392 [27]
Hawaii (Maui), 1982, (Cayenne)	360 SC	3.2 + 3.36 P	12 + 1	30	wet bran pulp crowns foliage	0.05 <u>≤0.01</u> 0.03 0.12	82393 [28]
Hawaii (Lanai), 1982, (Smooth Cayenne)	15 GR + 360 SC	22.4 + 2.24 + 3.36 P	1 + 1 + 7	27	foliage pulp bran	0.04 <u>≤0.01</u> <0.01	Mobay 1982h 80643 [29]
Hawaii (Maui), 1982, (Cayenne)	15 GR + 360 SC	22.4 + 3.17 + 3.36 P	1 + 6 + 1	30	foliage pulp bran	<0.01 <u>≤0.01</u> <0.01	80644 [30]

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
					crowns	<0.01	
Hawaii (Oahu), 1982, (Smooth Cayenne)	15 GR + 360 SC	22.4 + 3.36 + 2.24 P	1 + 6 + 1	36	foliage pulp bran crowns dried bran	0.06 <0.01 0.01 0.03 0.03	80645 [31]
Hawaii (Lanai), 1984, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	139	wet bran pulp foliage	<0.01 <0.01 <0.01	Mobay 1984a 88759 [32]
Hawaii (Lanai), 1984, (Smooth Cayenne)	360 SC	2.24 + 3.36 R	1 + 6	139	wet bran pulp foliage	<0.01 <0.01 0.03	88760 [32]
Hawaii (Maui), 1984, (Cayenne)	360 SC	22.4 + 2.1 + 3.36 P	1 + 9 + 1	30	wet bran pulp foliage	0.07 <0.01 0.10	88761 [33]
Hawaii (Lanai), 1984, (Smooth Cayenne)	15 GR + 360 SC	22.4 + 2.24 + 3.36 P	1 + 1 + 7	27	wet bran pulp foliage	0.09 <0.01 0.08 (*0.03 c*)	Mobay 1984b 88746 [34]
Hawaii (Lanai), 1984, (Smooth Cayenne)	15 GR + 360 SC	22.4 + 2.24 + 3.36 P	1 + 1 +7	27	wet bran pulp foliage	0.05 <0.01 0.18 (*0.03 c*)	88747 [34]
GAP							
Australia	**400 liq.**	2.4 (plant + ratoon)	**5**				
		4.8 (ratoon)	**2**				
US (Puerto Rico)	**15 GR**	10 (pre-plant)					
	350 EC	5.4-9.8 (post-plant, 1st ratoon)	**225**				
			Total application 20 kg ai/ha to ratoon crop.				
US (Hawaii)		9.8 (Pre-plant)	**Total application 26.2 kg ai/ha/plant crop**				
			Total application 9.8 kg ai/ratoon crop				
	350 EC	0.5-3.3 (post-plant)		**30**			

P: plant crop R: rotation crop

[1] Three applications: soil broadcast at 22.4 kg ai/ha with 10 GR 1 day before planting and two broadcast foliar sprays 156 and 308 days after planting. Limit of detection = 0.01 mg/kg.

[2] Three applications: soil broadcast at 22.4 kg ai/ha with 10 GR 8 days before planting and two broadcast foliar sprays 149 and 308 days after planting. Limit of detection = 0.01 mg/kg.

[3] Three applications: soil broadcast at 22.4 kg ai/ha with 10 GR 5 days before planting and two broadcast foliar sprays 150 and 305 days after planting. Limit of detection = 0.01 mg/kg.

[4] Three applications: soil broadcast at 22.4 kg ai/ha with 10 GR and two broadcast foliar sprays 187 and 376 days after planting. Limit of detection = 0.01 mg/kg.

[5] Three applications: one soil broadcast with 10 GR 1 day before planting and two broadcast foliar sprays with 3 LC 153 and 309 days after treatment. Limit of detection = 0.01 mg/kg.

[6] Five applications: one soil broadcast with 15 GR (pre-planting) and 4 foliar sprays with 3 SC 107, 213, 302 and 376 days after planting. Limit of detection = 0.01 mg/kg.

[7] Five applications: one soil broadcast with 15 GR (pre-planting) and 4 foliar sprays with 3 SC 107, 202, 287 and 381 days after planting. Limit of detection = 0.01 mg/kg.

[8] 7 applications: one soil broadcast with 15 GR (pre-planting) and 6 foliar sprays with 360 EC 96, 191, 276, 370, 495 and 559 days after planting. Limit of detection = 0.01 mg/kg.

[9] Seven applications: one soil broadcast with 15 GR (pre-planting) and 6 foliar sprays with 360 EC 98, 204, 294, 368, 462 and 546 days after planting. Limit of detection = 0.01 mg/kg.

[10] 5 sprays applied by knapsack 1, 92, 192, 271 and 377 days after planting. Limit of detection = 0.01 mg/kg, recovery at 0.05 mg/kg = 97%. No chromatograms provided.

[11] 4 applications: one pre-plant soil broadcast and incorporation with 15 GR and 3 foliar sprays at 92 day intervals. Limit of detection = 0.01 mg/kg.

[12] 6 foliar sprays 2 days before planting and 26, 92, 154, 216 and 288 days after planting. Limit of detection = 0.01 mg/kg.

[13] 8 foliar sprays to plant crop and ratoon crop; ratoon crop harvested for analysis. First application 111 days after planting; remaining applications 82, 195, 250, 343, 551, 641 and 735 days after the first application. Plant crop harvested between sprays 5 and 6. Plot size 32.5m^2. Limit of detection = 0.01 mg/kg.

[14] 4 sprays, first 88 days after planting, then 182, 276 and 348 days after planting. Limit of detection = 0.01 mg/kg.

[15] 4 sprays, first 85 days after planting, then 184, 269 and 354 days after planting. Limit of detection = 0.01 mg/kg. Plot size 32.5 m^2.
[16] 5 applications: one broadcast application at planting then foliar sprays 85, 184, 269 and 354 days after planting. Limit of detection = 0.01 mg/kg. Plot size 32.5 m^2.
[17] 9 applications. Initial pre-plant broadcast 15 days before planting, after applications by drip irrigation at vegetative stages (105, 181, 251, 328, 392, 462 days after planting), mid-cone stages, (532 days after planting) and last application at immature fruit stage (637 days after planting). Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[18] 8 applications. Initial broadcast spray with incorporation at planting, after applications by drip irrigation at vegetative stages (95, 180, 273, 376, days after planting), post-force stage (462 days), red cone stage (546 days) and immature fruit stage (625 days after planting). Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[19] 15 applications by drip irrigation. Initial application 73 days after planting, after applications at vegetative stages (105, 136, 181, 218, 251, 289, 329, 361, 393, 442, 463 days), early bud stage (498 days), mid cone (533 days) and immature fruit (638 days after planting). Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[20] 10 applications by drip irrigation. Initial application 29 days after planting, after applications at vegetative stages (63, 117, 178, 245, 301,374, 419), post-force (478 days), early petal (565 days), immature fruit (624 days after planting). Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[21] 8 applications by drip irrigation. Initial application 10 days before planting, after applications at vegetative stages (84, 96, 195, 280 days after planting), developing bud stage (353, 413 days) and maturing fruit stage (503 days after planting). Plot size 251 m^2. Limit of detection = 0.01 mg/kg.
[22] 7 applications by drip irrigation to ratoon crop. Initial application 709 days after planting; re-treatment at 30-41 day intervals at vegetative stages, post-force and early bud. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[23] 7 applications by drip irrigation to ratoon crop at 25-79 day intervals at vegetative stages, force, developing bud and immature fruit stages. Plot size 251 m^2. Limit of detection = 0.01 mg/kg.
[24] 8 applications by drip irrigation to 1st ratoon crop at 20-71 day intervals at vegetative stages, developing bud stage and maturing fruit stages. Plot size 227 m^2. Limit of detection = 0.01 mg/kg.
[25] 6 applications by drip irrigation to 2nd ratoon crop at 13-47 day intervals at developing bud and maturing fruit stages. Plot size 227 m^2. Limit of detection = 0.01 mg/kg.
[26] 15 applications by broadcast foliar spray to plant crop. Initial application 58 days after planting then at 35-53 day intervals at vegetative, early bud, mid-cone, flowering and immature fruit stages. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[27] 7 applications by broadcast foliar spray to ratoon crop. Applications at 34-79 day intervals at vegetative, post-force and early bud stages. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[28] 12 applications by broadcast foliar spray. Initial application 27 days after planting, then at vegetative stages (63, 92, 119, 155, 180, 210, 245, 274 and 303 days), post-force 376 days, early petal 412 days and immature fruit, 626 days after planting. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[29] 9 applications. Initial broadcast and incorporation with 15 GR 15 days before planting, then application by drip irrigation at vegetative stages (105, 181, 251, 328, 392, 462 days), mid-cone 532 days, and immature fruit 637 days after planting. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[30] 8 applications. Initial application by broadcast and incorporation at planting with 15 GR, then application by drip irrigation with 360 SC at vegetative stages (95, 180, 274, 376 days post-force 462, red cone 547, immature fruit 626 days after planting. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[31] 8 applications. Initial application by broadcast and incorporation with 15 GR 7 days before planting, then application by drip irrigation with 360 SC at vegetative stages (95, 194, 279 days), developing bud 352 and 412 days and maturing fruit 471 and 592 days after planting. Plot size 251 m^2. Limit of detection = 0.01 mg/kg.
[32] 7 applications by drip irrigation at intervals of 34-41 days. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[33] 11 applications. Initial broadcast spray and incorporation at planting, then at vegetative stages (63, 117, 178, 243, 301, 374, 419 days), post-force 478, early petal 575, immature fruit 624 days after planting. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.
[34] 9 applications. Initial broadcast and incorporation 11 days before planting, then at pre-bud stage 58, 163, 233, 303, 373 days, early bud stage 443 days, flowering 513 days, 596 days late immature fruit stages. Plot size 30.2 m^2. Limit of detection = 0.01 mg/kg.

The residues in whole fruit were <0.01 mg/kg in the three Australian trials, but only one trial was in accordance with GAP. In the trials in Puerto Rico the residues were <0.01 mg/kg in the pulp. All of the Hawaiian trials were at excessive rates of 1.2-2.3 times the total plant crop application rate and up to 2.3 times the total ratoon crop rate. Pre-planting applications were at 2.3 times the prescribed rate in all of the Hawaiian trials. The residues were <0.01-0.03 mg/kg in whole fruit and <0.01-0.05 mg/kg in pulp from these exaggerated treatments.

The residues in products used for animal feed were <0.01-8.68 mg/kg in foliage, <0.01-0.71 mg/kg in wet bran, <0.01-2.27 mg/kg in crowns, <0.02-0.02 mg/kg in dry bran and <0.01-0.13 mg/kg in stumps. Additional results are shown in Table 99 in pineapple processing trials. In a pineapple metabolism study (Flint, 1973) the total radioactive residues in fruit 30 days after soil treatment at 22.4 kg ai/ha were less than 10 ng/g (ppb) fenamiphos equivalents or fenamiphos phenol equivalents.

Peanuts. In trials in the USA and South Africa (Table 87) fenamiphos was applied at planting and samples were taken at normal harvest. The residues were determined in animal feed commodities such as vines, foliage and shells, in addition to the edible kernels. The dry matter contents of vines, foliage and dry foliage were not reported. Chromatograms were provided unless otherwise stated. Recoveries were determined at 0.1 mg/kg in peanut hulls and kernels and at 0.5 mg/kg in vines (Table 61).

Table 87. Residues in peanuts, peanut shells and vines from trials in South Africa and the USA.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
USA (Texas), 1970, (Starr)	10 GR	13.4	1	125	nuts shells vines	<0.01 0.04 0.50	Chemagro 1970c 27020 [1]
USA (Nth Carolina), 1970, (NC-5)	10 GR	13.4	1	152 94	nuts shells vines	<0.01 <0.01 <0.01	27021 [1]
USA (Virginia), 1970, (Flori Giant)	10 GR	13.4	1	139	nuts shells vines	<0.01 0.05 0.94	27022 [1]
USA (Texas), 1970, (Starr)	10 GR	20.16	1	125	nuts shells vines	<0.01 0.02 2.05	27026 [1]
USA (Nth Carolina), 1970, (NC-5)	10 GR	13.4	1	153	nuts shells vines	<0.01 0.04 0.23	27028 [1]
USA (Mississippi), 1970, (Tennessee Red)	10 GR	13.4	1	140	nuts shells vines	<0.01 <0.01 0.41	27029 [1]
USA (Mississippi), 1970, (Tennessee Red)	10 GR	20.16	1	140	nuts shells vines	<0.01 0.02 0.21	27031 [1]
USA (Texas), 1970, (Starr)	3 SC	13.4	1	125	nuts shells vines	<0.01 0.01 1.89	Chemagro 1970d 27016 [1]
USA (Mississippi), 1970, (Tennessee Red)	3 SC	13.4	1	140	nuts shells vines	<0.01 <0.01 0.02	27017 [1]
USA (Mississippi), 1970, (Tennessee Red)	3 SC	20.16	1	140	nuts shells vines	<0.01 <0.01 0.04	27018 [1]
USA (Virginia), 1970, (Flori Giant)	3 SC	13.4	1	139	nuts shells vines	<0.01 <0.01 0.18	27019 [1]
USA (Nth Carolina), 1970, (NC-5)	3 SC	13.4	1	154	nuts shells vines	<0.01 0.31 0.20	27032 [2]
USA (Nth Carolina), 1970, (NC-5)	3 SC	13.4	1	148	nuts shells vines	<0.01 <0.01 0.02	27033 [1]
USA (Texas), 1970, (Starr)	3 SC	13.4	1	125	nuts shells vines	<0.01 <0.01 3.19	27035 [1]
South Africa (Nth Cape), 1990, (Nordan)	400 EC	1.6 2.4 3.2	1 1 1	68 68 68	nuts foliage nuts foliage nuts foliage	<0.04, <0.04 <0.04, <0.04 <0.04, <0.04 <0.04, <0.04 <0.04, <0.04 0.04, 0.05	S. Afr. Bur. Stds.1990b 311/88899/G361 [3]
South Africa (Transvaal), 1992, (Selly)	400 EC	1.6	1	63 76 90	whole plant foliage nuts foliage nuts	<0.04, <0.04 <0.04, <0.04 <0.04, <0.04 <0.04, <0.04 <0.04, <0.04	S. Afr. Bur. Stds.1994 311/88529/K102 [4]

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
				104	foliage	<0.04, <0.04	
					nuts	<0.04, <0.04	
				116	dry foliage	<0.04, <0.04	
					nuts	<0.04, <0.04	
					shells	<0.04, <0.04	
		3.2	1	63	whole plant	<0.04, <0.04	
				76	foliage	<0.04, <0.04	
					nuts	<0.04, <0.04	
				90	foliage	<0.04, <0.04	
					nuts	<0.04, <0.04	
				104	foliage	<0.04, <0.04	
					nuts	<0.04, <0.04	
				116	dry foliage	<0.04, <0.04	
					nuts	<0.04, <0.04	
					shells	<0.04, <0.04	
GAP							
South Africa	**400 EC**	**1.6-3.2**	**1**	**63**			
USA	**15 GR**	**1.68-2.85**	**1**				
	400 EC	**1.63-2.70**	**1**				

[1] Single broadcast application with incorporation in soil. Limit of detection = 0.01 mg/kg.
[2] Single broadcast application with incorporation in soil. Limit of detection = 0.01 mg/kg. Recovery at 0.1 mg/kg = 92%.
[3] Single application at planting by tractor mounted applicator. Plot size 2800 m^2, sandy loam soil, pH 6. Foliage samples included leaves and pods. Recovery at 0.1 mg/kg of F, FSO and FSO_2 = 84, 60 and 92% respectively from nuts, 67, 61 and 100% from foliage or whole plant. No chromatograms provided.
[4] Single application by high volume spray. Plot size 815 m^2, soil composition: 24% clay, 7% silt and 69% sand; pH 7.6, 0.43% C. Whole plant samples included foliage and pods. Limit of detection = 0.04 mg/kg. Recovery of F, FSO and FSO_2 63, 66 and 90% from dry foliage and 77, 74 and 90% from shells at 0.04 mg/kg, 81, 100 and 88% from foliage at 0.05 mg/kg and 75, 61 and 72% at 0.1 mg/kg, 67, 95 and 76% from dry foliage and 76, 76 and 69% from nuts at 0.2 mg/kg, and 82, 73 and 67% from nuts at 0.08 mg/kg.

Although up to 7 times the registered rate was applied in the US trials the residues in nuts were <0.01 mg/kg at the earliest harvest intervals. The residues in vines were <0.01-3.19 mg/kg at 4.7-7 times the registered rate after 94-154 days.

Cotton. The results of supervised trials in South Africa, Brazil and the USA are shown in Table 88. In all the trials fenamiphos was applied either before or shortly after planting and cotton seed, gin trash and foliage samples were collected at normal harvest. Recoveries from cotton seed fortified at 0.05 mg/kg were recorded in Table 61.

Table 88. Results of supervised field trials on cotton in the USA, Brazil and South Africa.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference.
	Form.	kg ai/ha	No.				
USA (Oklahoma), 1971, (Lankburn)	15 GR	4.06	1	161	seed gin trash	<0.01 <0.01	Chemagro 1971a 29981 [1]
USA (Arkansas), 1971,	15 GR	3.66	1	163	seed	<0.01	30027 [2]
(Stoneville 213)					gin trash	<0.01	
				148	foliage	0.10	
USA (Louisiana), 1971, (D.P.L. Smooth Leaf)	15 GR	3.66	1	196	seed gin trash	<0.01 <0.01	30028 [2]
USA (California), 1971, (Delta Pine)	15 GR	3.85	1	157	seed foliage	<0.01 <0.01	30031 [3]
USA (Louisiana), 1971, (D.P.L. Smooth Leaf)	15 GR	5.50	1	196	seed gin trash	<0.01 <0.01	30032 [1]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference.
	Form.	kg ai/ha	No.	days		mg/kg	
USA (California), 1971, (Delta Pine)	3 SC	3.85	1	157 142	seed foliage	<0.01 <0.01	Chemagro 1971b 30025 [3]
USA (Louisiana), 1971, (D.P.L. Smooth Leaf)	3 SC	3.66	1	196	seed gin trash	<0.01 <0.01	30026 [2]
USA (Louisiana), 1971, (D.P.L. Smooth Leaf)	3 SC	5.5	1	196	seed gin trash	<0.01 <0.01	30029 [4]
USA (Arkansas), 1971, (Stoneville)	3 SC	3.65	1	163 148	seed gin trash foliage	<0.01 <0.01 0.04	30030 [2]
USA (Oklahoma), 1971, (Lankburn)	3 SC	4.06	1	161	seed gin trash	<0.01 <0.01	30033 [1]
USA (Arizona), 1977, (D & PL 16)	15 GR	1.83	1	155	seed	<0.01	Chemagro 1977b 52992 [5]
USA (Texas), 1977, (SP 37)	15 GR	5.59	1	131	seed	<0.01	52993 [6]
USA (Arizona), 1977, (DPL 16)	15 GR	3.65	1	155	seed	<0.01	52994 [7]
USA (Sth Carolina), 1977, (Coker 201)	15 GR	2.04	1	145	seed	0.05 (*0.03 c*)	53118 [8]
USA (Texas), 1977, (SP 37)	3 SC	3.68	1	131	seed	<0.01	Chemagro 1977c 52995 [9]
USA (Texas), 1977, (Lockett 4789A)	3 SC	3.68	1	183	seed	<0.01	52996 [10]
USA (Arizona), 1977, (DPL 16)	3 SC	3.65	1	155	seed	<0.01	52997 [7]
USA (Texas), 1977, (SP 37)	3 SC	5.59	1	130	seed	<0.01	52998 [6]
USA (Arizona), 1977, (DPL 16)	3 SC	5.5	1	155	seed	<0.01	52999 [4]
USA (Sth Carolina), 1977, (Coker 201)	3 SC	2.04	1	145	seed	0.04 (*0.03 c*)	53117 [11]
USA (Mississippi), 1979, (Stoneville 213)	15 GR	1.93	1	147	seed	<0.01	Mobay 1979c 66865 [12]
USA (Mississippi), 1979, (Stoneville 213)	15 GR	2.89	1	147	seed	<0.01	66866 [13]
USA (Mississippi), 1979, (Stoneville 213)	3 SC	1.92	1	147	seed	<0.01	Mobay 1979d 66867 [11]
USA (Mississippi), 1979, (Stoneville 213)	3 SC	2.89	1	147	seed	<0.01	66868 [13]
Brazil, (Rolandia), 1987, (IAC-20)	10 GR	4 g ai/plant	1	92 120 147	boll fuzzy seed fuzzy seed	<0.2 <0.2 <0.2	U. de Sao Paulo 1988b BRA-1004-88-A [14]
Brazil (Rolandia), 1987, (IAC-20)	10 GR	8 g ai/plant	1	120	fuzzy seed	<0.2	BRA-1004-88-B [15]
South Africa (Nth Cape), 1989, (Acala)	400 EC	4	1	126 195 210	delinted seed	<0.05, <0.05 <0.05, <0.05 <0.05, <0.05	S. Afr. Bur. Stds. 1990c 311/88944/G528 [16]
South Africa (Nth Cape), 1989, (Acala)	400 EC	4	1	126 195 210	delinted seed	<0.05, <0.05 <0.05, <0.05 <0.05, <0.05	311/88900/G362 [17]
GAP **Brazil** **South Africa**	 **10 GR** **10 GR**	 **3-5** **15 g ai/100 m row**	**1**	**98**			
USA	**15 GR** **350 EC**	**0.84-1.65** **0.82-3.27**					

[1] Application in 30.5 cm band with incorporation at planting (0.375 g/m row, 91 cm row spacing). Limit of detection = 0.01 mg/kg.

[2] Application in 30.5 cm band with incorporation at planting (0.375 g/m row, 102 cm row spacing). Limit of detection = 0.01 mg/kg.
[3] Application in 30.5 cm band with incorporation at planting (0.375 g/m row, 96.5 cm row spacing). Limit of detection = 0.01 mg/kg.
[4] Application as a band in-furrow at planting (0.56 g/m row, 102 cm row spacing). Limit of detection = 0.01 mg/kg.
[5] Application in 15.2 cm band at planting (0.19 g/m row, 102 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[6] Application in 15.2 cm band at planting (0.28 g/m row, 51 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[7] Application in 15.2 cm band at planting (0.375 g/m row, 102 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[8] Application in 15.2 cm band at planting (0.19 g/m row, 102 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[9] Application in 15.2 cm band at planting (0.19 g/m row, 51 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[10] Application in 10.2 cm band at planting (0.19 g/m row, 51 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[11] Application in 15.2 cm band at planting (0.19 g/m row, 91 cm row spacing). Limit of detection = 0.01 mg/kg. No chromatograms provided.
[12] Applied in 10 to 15.2 cm band at planting (0.19 g/m row, 96.5 cm row spacing). Plot size 1486 m^2. Limit of detection = 0.01 mg/kg. No chromatograms provided.
[13] Applied in 10 to 15.2 cm band at planting (0.28 g/m row, 96.5 cm row spacing). Plot size 1486 m^2. Limit of detection = 0.01 mg/kg. No chromatograms provided.
[14] Application by spreading at planting. Plot size 120 m^2, clay soil, pH 6.2, 4% C. Recovery at 0.2 mg/kg 74-80%.
[15] Application by spreading at planting. Plot size 80 m^2, clay soil, pH 6.2, 4% C. Recovery at 0.2 mg/kg 74-80%.
[16] Applied by pivot irrigation at planting. Plot size 2.5 ha, sandy loam soil, pH 5.8. Limit of detection = 0.05 mg/kg. Recovery at 0.1 mg/kg = 89, 100 and 83% of F, FSO and FSO_2 respectively. No chromatograms provided.
[17] Applied by pivot irrigation at planting. Plot size 2 ha, sandy loam soil, pH 5.5. Limit of detection = 0.05 mg/kg. Recovery at 0.1 mg/kg = 89, 100 and 83% of F, FSO and FSO_2 respectively. No chromatograms provided.

The residues in cotton seed were below the limit of detection or determination in many of the trials. Residues above the limit of detection were found in 2 cotton seed samples but also in the corresponding controls. Residues were present in foliage in some trials where the foliage was sampled before harvest of the seed.

Coffee. Trials were conducted in Guatemala, Brazil and Mexico (Table 89). A single soil application of fenamiphos was made to mature trees at pre-bloom or fruit formation. Residues were determined in the berries and beans. The MRLs apply to the seed (bean) only.

Table 89. Residues in coffee berries and beans from trials in Guatemala, Brazil and Mexico.

Location, year, (variety)	Application			PHI, days	Sample	Residues, mg/kg	Reference
	Form.	kg ai/ha	No.				
Guatemala, (Escuintla), 1978, (Bourbon)	10 GR	2.5 g ai/plant	1	30	bean	<0.1	Inst. Nut. Cent. Amer.y Panama 1978 GUA-78-2-13-A [1]
Guatemala (Escuintla), 1978, (Bourbon)	10 GR	2.5 g ai/plant	1	45	bean	<0.1	GUA-78-2-13-B [1]
Guatemala (Escuintla), 1978, (Bourbon)	10 GR	2.5 g ai/plant	1	60	bean	<0.1	GUA-78-2-13-C [1]
Guatemala (Escuintla), 1978, (Bourbon)	10 GR	2.5 g ai/plant	1	90	bean	<0.1	GUA-78-2-13-D [1]
Brazil (Sao Paulo), 1988, (Catuai)	10 GR	7 g ai/plant	2	30 45 60	bean	<0.2 <0.2 <0.2	U. de Sao Paulo 1988c BRA-1002-88-A [2]
Brazil (Sao Paulo), 1988, (Catuai)	10 GR	14 g ai/plant	2	45	bean	<0.2	BRA-1002-88-B [3]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	4 2	1 1	60 60	berry berry	<0.05 0.04	Bayer 1986d 0021-86-A [4]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	4 2	1 1	45 45	berry berry	<0.05 0.03	0021-86-B [4]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	4 2	1 1	30 30	berry berry	<0.05 0.01	0021-86-C [4]

Location, year, (variety)	Application			PHI,	Sample	Residues,	Reference
	Form.	kg ai/ha	No.	days		mg/kg	
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	4 2	1 1	15 15	berry berry	<0.05 0.02	0021-86-D [4]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	8 4	1 1	60 60	berry berry	<0.05 0.01	Bayer 1986e 0035-86-A [4]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	8 4	1 1	45 45	berry berry	<0.05 0.11	0035-86-B [4]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	8 4	1 1	30 30	berry berry	<0.05 0.06	0035-86-C [4]
Guatemala (Mazatenango) 1986, (Caturra)	12 GR	8 4	1 1	15 15	berry berry	<0.05 0.01	0035-86-D [4]
Mexico (Coatepec), 1988, (Mundo Nuevo)	15 GR	1.5 g ai/m tree height	1	123 154	bean	<0.01 0.09	Leslie 1988b 96780 MEX-3900-81H [5]
Mexico (Coatepec), 1988, (Garnica)	15 GR	1.5 g ai/m tree height	1	123 154	bean	<0.01 0.04	MEX-3901-81H [5]
Mexico (Xico), 1984, (Garnica)	15 GR	1.5 g ai/m tree height	1	122 153	bean	<0.01 0.08	MEX-3902-81H [5]
Mexico (Xico), 1984, (Mundo Nuevo)	15 GR	1.5 g ai/m tree height	1	123 154	bean	<0.01 0.10	MEX-3903-81H [5]
GAP							
Brazil	**10 GR**	**1– 1.5 g ai/plant 7 g ai/plant**	**3**	**45**			
Guatemala	**10 GR 12 GR 15 GR**	**5 2.4-3.6 5.1**	**1**	**60**			
Mexico	**10 GR**	**1-1.5 g ai/plant**	**1**	**45**			

[1] Single application by spreading around trunks at fruit development. Plot size 15 plants. Limit of determination = 0.1 mg/kg. No chromatograms provided.
[2] Two applications at 49 day interval with final application at the beginning of fruit ripening. Applied by spreading. Plot size 40 plants, clay soil, pH 5.7, 1.68% C. Limit of determination = 0.2 mg/kg, recoveries at 0.2 mg/kg 77-87%. No chromatograms provided.
[3] Two applications at 49 day interval with final application at the beginning of fruit ripening. Applied by spreading. Plot size 20 plants, clay soil, pH 5.7, 1.68% C. Limit of determination = 0.2 mg/kg, recoveries at 0.2 mg/kg 77-87%. No chromatograms provided.
[4] Single application by spreading. Plot 132 m^2, loamy soil, pH 5.6, 6.8% C. Limit of determination = 0.05 mg/kg., recovery at 0.05 mg/kg = 72%. No chromatograms provided.
[5] Single in-furrow application at pre-bloom stage around tree at drip line. Plot size 54 m^2, silty clay soil, pH 5.5-6.4, 3-4% C. Recoveries of F, FSO and FOS_2 at 0.05 mg/kg = 86, 70 and 78% respectively. Recoveries of F at 0.1 mg/kg = 79 and 86%, and at 0.5 mg/kg = 77%.

The residues in the Guatemala trials were <0.01-<0.02 mg/kg in the beans from the 10 GR and 0.01-0.11 mg/kg in the berries from the 12 GR product. The Mexican application rates were expressed in terms of g ai/tree height.

Animal feeding studies

Alfalfa pellets containing fenamiphos sulfoxide were fed to dairy cattle for 28 days at levels equivalent to 2, 6 and 20 ppm in the diet (Wargo, 1978). The sulfoxide was used as it was considered to be the major component of the residues found in treated crops which may be used as animal feed items. The feed levels equated to 44, 151 and 493 mg/kg bw/day for an average feed intake of 15 kg/animal/day and the average body weight of each group. There were 3 cows in each treatment group and one control animal. Blood samples were taken on days 0, 7, 14, 21 and 28 of the trial and cholinesterase activity was compared with that in blood taken at 3 intervals in the 7 days before dosing.

The cows were milked in the morning and evening and samples of milk from the cows in each group for each day were composited for analysis. On day 29 the animals were killed and samples of

liver, kidney, muscle (flank and loin), and fat (omental, subcutaneous and renal) were extracted for analysis less than 24 hours after death. The limit of detection was reported as 0.001 mg/kg in the milk and 0.01 mg/kg in the tissues.

Cholinesterase activity was not reduced after feeding at the 2 and 6 ppm levels, but significant depression of activity was noted by day 21 at 20 ppm.

The residues were <0.001 mg/kg in all milk samples taken from the highest dose group. Residues in the liver were ≤0.01 mg/kg in the 6 ppm group and <0.01 to 0.012 mg/kg in the 20 ppm group (levels of 0.011-0.012 mg/kg were found in 1 of the 3 animals). In the kidneys, composite fat and muscle taken from the 20 ppm group, residues were all <0.01 mg/kg.

Groups of 4 laying hens were fed for 14 consecutive days with [U-*phenyl*-^{14}C]fenamiphos at 0, 0.06, 0.18 and 0.65 ppm incorporated into the feed each morning (Gronberg *et al.,* 1973). The feed concentrations corresponded to average intakes of 3.42, 10.18 and 37.96 µg fenamiphos/kg bw/day. Eggs were collected each morning and the hens were killed after 14 days for the analysis of blood, brain, skin, muscle, heart, liver, gizzard, kidney and fat.

The radioactive residues in eggs reached maximum levels after 7 days feeding in all groups. The limit of detection in eggs was reported as 0.003 mg/kg. Residues in the tissues of the high-dose group are shown in Table 90.

Table 90. Total radioactive residues in hen tissues and blood after feeding at 0.65 ppm (Gronberg *et al.,* 1973).

Sample	TRR, µg/kg as fenamiphos
Brain	2.58
Heart	5.32
Liver	4.51
Kidney	4.70
Muscle	2.76
Fat	2.96
Gizzard	4.22
Skin	2.46
Whole blood	3.90

The highest radioactive residues were found in heart, kidney, liver and gizzard.

In a subsequent trial (Bell *et al.,* 1974), groups of four laying hens were fed for 14 consecutive days with [U-*phenyl*-^{14}C]fenamiphos at 2, 4 and 100 ppm in the feed, corresponding to average concentrations of 0.12, 0.28 and 0.76 mg fenamiphos/kg bw/day. Eggs were collected each morning and samples of brain, liver, kidney, fat, gizzard, heart, and white and dark muscle were collected at death.

The total radioactivity in eggs reached maximum levels after 6 days feeding in all groups, similar to the 7 days found in the Gronberg study. The maximum residues in the tissues were below the minimum quantifiable limits (7-20 µg/kg) in the 2 and 4 ppm groups. At the 10 ppm feeding level, residues of 47, 27 and 18 µg/kg were present in the gizzard, kidneys and liver respectively.

Estimation of dietary burden for livestock

Estimates of the exposure of cattle and hens to fenamiphos residues in treated feed items are shown in Tables 91 and 92, together with the estimated maximum and median residues in animal feed commodities. All median residues have been estimated from the results of trials which were considered to be according to GAP. Items for which intake figures were not available but which may be used in animal feed have also been included. The main contributions to the intake are shown bold. For cattle an intake of 15 kg dry matter/day is assumed, with an average body weight of 500 kg.

Table 91. Estimated dietary burden for dairy cattle.

Commodity	Maximum residue, mg/kg	Median residue, mg/kg	% in the feed	% DM	Intake, mg/animal/day
Citrus peel	0.71	0.06	20		0.18
Citrus pulp		0.01	20		0.03
Apple pomace, dry		0.18	40		**1.08**
Grape pomace, dry		0.1	20		0.3
Raisin trash		0.15	20		**0.45**
Peanut meal		0.01	15		0.02
Peanut vines	0.05	0.04	25	85	**0.15**
Cotton seed	<0.01	<0.01	25	88	<0.038
Cotton hulls		0.01	20	89	0.03
Cotton meal		0.01	15		0.02
Gin by-products		<0.01	20		0.03
Tomato pulp, dry		0.13	10		**0.195**
Tomato pomace		0.12	10		0.18
Pineapple wet bran	1.07	<0.01			
Pineapple dry bran	2.60	<0.01	30		0.045
Pineapple foliage	8.68	0.04			
Pineapple crowns	2.27	<0.01			
Cabbage trash	0.19				

The total exposure from a diet composed of the items providing the highest median intake (dry apple pomace, raisin trash, peanut vines and dry tomato pulp) is 1.875 mg/animal/day or 0.125 ppm in the feed (0.004 mg/kg bw/day). The lowest feed level in the cattle trial reported by Wargo (1978) was 2 ppm fenamiphos sulfoxide, or about 15 times the estimated intake.

The intake for hens was estimated assuming an average body weight of 2 kg and an intake of 150 g dry matter/day.

Table 92. Estimated dietary burden for laying hens.

Commodity	Maximum residue, mg/kg	Median residue, mg/kg	% in the feed	% DM	Intake, mg/animal/day
Cotton meal		0.01	20		**0.0003**
Peanut meal		0.01	25		**0.0003**

Assuming 100% intake of peanut meal, hens would be exposed to 0.01 ppm in the feed. The lowest feed level in the reported hen feeding studies was 0.06 ppm of [U-*phenyl*-^{14}C]fenamiphos (Gronberg *et al.*, 1973). The total radioactive residues in the tissues and eggs were reported without characterization of the radioactivity. In a subsequent feeding study (Bell *et al.*, 1974) the maximum residues in the tissues were below 20 µg/kg after feeding at the 2 ppm level.

FATE OF RESIDUES IN STORAGE AND PROCESSING

Processing studies with tomatoes, oranges, apples, grapes and pineapples were reported.

Tomatoes. Whole tomatoes containing 0.5 mg/kg fenamiphos were subjected to commercial processing into canned tomatoes, pasteurised juice and ketchup (Morris, 1975). The residues in the processed fractions and the corresponding processing factors are shown in Table 93.

Table 93. Residues and processing factors from a tomato processing trial (Morris, 1975).

Sample	Residue, mg/kg	Processing factor
Whole tomatoes	0.50	NA
Pasteurised tomato juice	0.44	0.88
Sterilized tomatoes (canned)	0.36	0.72
Tomato ketchup	0.29	0.58
Tomato juice	0.37	0.74

Sample	Residue, mg/kg	Processing factor
Tomato pulp solids	0.52	1.04s
Dry tomato seeds and fibres	0.79	1.58
Dry tomato peels and cores	1.89	3.78
Dry tomato pulp solids	3.12	6.24
Dry tomato pomace	1.25	2.5

The recoveries of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone at 0.1 mg/kg were 100, 100 and 101% respectively in whole tomatoes, 91, 93 and 92% in ketchup, and 107, 84 and 84% in dried tomato pulp.

In another study (Simmons and Thornton, 1975), raw tomatoes were fortified with [U-*phenyl*-^{14}C]fenamiphos sulfoxide at a concentration of 0.8 mg/kg. The tomatoes were allowed to stand at room temperature for 24 hours, then blanched, peeled, cored and cooked in canning jars for 40 minutes. The jars were cooled and the fractions analysed for radioactive residues.

The residues were extracted into organic solvents and the organosoluble radioactivity was distributed among the fractions as shown in Table 94.

Table 94. Distribution of radioactive residues in tomatoes fortified with [^{14}C]fenamiphos sulfoxide and their processed fractions (Simmons and Thornton, 1975).

Sample	Total ^{14}C*	FSO**	FSO_2**	FPSO**	$FPSO_2$**
Blanching water	3.7 (0.03)	96.7 (0.03)	2.3 (<0.001)	0.9 (0.0003)	0.15 (<0.001)
Cooking water	23.4 (0.19)	95.3 (0.143)	2.6 (0.004)	0.7 (0.001)	0.09
Peels and cores	1.5 (0.01)	83.6 (0.009)	6.4 (<0.001)	6.5 (<0.001)	3.5 (<0.001)
Tomatoes	54.3 (0.44)	97 (0.41)		0.9 (0.004)	2.0 (0.008)
Filter paper	0.2 (0.002)				

* % of total applied ^{14}C and (mg/kg as FSO)
** % of ^{14}C in organic extract and (mg/kg as FSO).

The results indicate that the organosoluble radioactivity was largely unchanged fenamiphos sulfoxide and that the cooking process leads to little chemical change. Blanching and cooking reduced the residues in the tomatoes by almost 50%, with 27% present in the blanching and cooking water. There was negligible loss by removing peels and cores.

Oranges. Oranges trees were treated with Nemacur 15% granular at a rate equivalent to 100 kg ai/ha (Thornton, 1976). Leaves were taken at monthly intervals to determine when peak residues had moved systemically into the upper parts of the trees. When residues had reached plateau levels in the leaves, fruit were harvested and processed. The commercial processing procedure commenced with a pre-rinse wash, scrubbing with soap and water and an after-wash rinse.

The separate fractions analysed included the rinse waters, juice, peel, pulp, orange oil, dried peel and molasses. The residue data and corresponding processing factors are shown in Table 95. The residues in whole fruit were <0.01 to 0.13 mg/kg (average 0.07 mg/kg). Recoveries were determined in several fractions and are shown in Table 61.

Samples of oranges were held in frozen storage for 578 or 579 days with 15% degradation of fenamiphos and 13% degradation of fenamiphos sulfoxide. There was no observed degradation of fenamiphos sulfone.

Table 95. Residues in processed fractions of oranges and processing factors (Thornton, 1976).

Sample	Residue, mg/kg	Processing factor
Whole fruit	0.07	-
Peel (unwashed)	0.47	6.71
Pulp (unwashed)	<0.01	0.14

Sample	Residue, mg/kg	Processing factor
Peel (washed)	0.60	8.57
Pulp (washed)	0.01	0.14
Juice	0.02	0.28
Finisher pulp	0.02	0.28
Peel bits	0.23	3.28
Clear oil	4.48	64
Chopped peel	0.13	1.86
Pressed dry peel	0.40	5.71
Press liquor	0.20	2.85
Molasses	0.49	7

The concentration of residues was greatest in clear oil. Residues were also concentrated in peel and dried peel, both of which are used as cattle feed. Drying peel reduced the total residues by approximately 20%, but the loss of water was greater. Residues in the pulp and juice were negligible.

Apples. Apple trees were treated with a single soil broadcast application of Nemacur 3 SC at a rate equivalent to 33.6 kg ai/ha (Chemagro, 1976e). Fruit were harvested 66 days after treatment and processed into juice and pomace.

Table 96. Effect of processing on residues in apples.

Sample	Residue, mg/kg	Processing factor*
Whole fruit	0.14	
Wet pomace	0.80, 0.57; average 0.68	4.85
Dry pomace	2.66, 2.31; average 2.48	17.7
Juice	0.11, 0.11	0.78

* Calculated from average residues in processed fractions.

Residues were concentrated in wet and dry pomace, both of which are used as animal feed. The residues in apple juice were lower than those in the whole apples. Chromatograms were provided but recoveries were not reported.

Grapes. Processing studies were conducted in the USA. The results are shown in Tables 97 and 98.

The soil around grape vines was treated with three sprays of Nemacur 360 EC at a rate equivalent to 6.72 kg ai/ha (Mobay, 1981d, reports 69745 and 80080), the first at blooming, with 13-14 day intervals. The sprays were incorporated into the soil after application by hand sprayer.

In a processing trial in California (Grace, 1989, report 99611) Nemacur 3 EC was applied twice at a 6-week interval at a rate equivalent to 25.2 kg ai/ha (5 times the normal rate) as band sprays with incorporation. Samples of grapes, grape juice and wet pomace were collected 7 days after the second spray.

Table 97. Effect of processing on residues in Thompson Seedless grapes, California, USA.

Year	Application			PHI, days	Sample	Residues, mg/kg	Report no.
	Form.	kg ai/ha	No.				
1981	360 EC	6.72	3	55	whole fruit	0.07	69745 [1]
				70		0.05	
				80		0.04	
				55	Raisins, sun-dried	0.07	
				70		0.01	
				80		0.02	
				55	raisin trash, sun-dried	0.77	
				70		0.11	
				80		0.06	
				55	raisins, oven-dried	0.09	

Year	Application			PHI,	Sample	Residues,	Report no.
	Form.	kg ai/ha	No.	days		mg/kg	
				70		<0.01	
				80		<0.01	
				55	raisin trash, oven-dried	0.12	
				70		0.12	
				80		0.10	
1981	360 EC	6.72	3	56	whole fruit	0.02	80080 [2]
				73		0.01	
				56	raisins, sun-dried	0.03	
				73		0.01	
				56	raisin trash*	0.22	
				73		0.09	
				56	raisins, oven-dried	0.03	
				73		0.02	
				56	raisin trash, oven-dried	0.19	
				73		0.13	
1988	360 EC	25.2	2	7	whole fruit	0.02	99611 [3]
					wet pomace	0.02	
					dry pomace	0.10	
					juice	0.02	

[1] 3 applications (14-day intervals) starting at blooming, by hand sprayer followed by incorporation. Plot size 74.2 m^2.
[2] 3 applications (49 and 36 days intervals) by broadcast spray to soil at 5-10 cm shoots, blooming and post-bloom. Plot size 39.9 m^2.
[3] Two band sprays to soil near vines with incorporation at 42-day interval, 1st spray near maturity and 2nd spray at mature ripe fruit stage; plot size 17.8 m^2, sandy loam soil, pH 6.5-7.5, <1% C. Limit of determination = 0.01 mg/kg. Recoveries from fruit were F 102, 91%, FSO 76, 83% and FSO_2 81, 102% at 0.01 mg/kg; F 82 %, FSO 75%, and FSO_2 95% at 0.02 mg/kg; F 72%, FSO 76%, FSO_2 94% at 0.1 mg/kg. Recoveries from juice were F 99%, FSO 86% and FSO_2 91% at 0.1 mg/kg, from wet pomace F 74, 101%, FSO 75, 84%, FSO_2 83, 90% at 0.05 mg/kg, and from dry pomace F 75% at 0.1 mg/kg.

Table 98. Effect of processing on residues in grapes and mean processing factors for processed fractions.

Sample	Residue, mg/kg	Processing factor[1]	Report no.
Whole fruit (PHI 55/56 days)	0.07, 0.02 (average 0.045)		69745, 80080
Raisins	0.07, 0.09, 0.03, 0.03 (average 0.055)	1.22	
Raisin trash	0.77, 0.12, 0.22, 0.19 (average 0.33)	7.33	
Whole fruit (PHI 7 days)	0.02		99611
Wet pomace	0.02	1	
Dry pomace	0.10	5	
Juice	0.02	1	

[1] (Mean residue in processed fraction) ÷ (mean residue in whole fruit)

The residues were concentrated in raisins and raisin waste, and in dry pomace after juicing and drying. The residues in juice and wet pomace did not differ from those in the whole fruit. Raisin waste and pomace are used as animal feed.

Pineapples. A processing trial was conducted in Wahiwa, Hawaii (Leslie, 1989a). One year-old pineapple plants were treated with 7 sprays of Nemacur 3 EC at a rate equivalent to 16.8 kg ai/ha (5 times the recommended rate) at 14- to 30-day intervals. Samples of mature pineapples were collected 14 days after the last application and the fruit were processed into raw and dried bran and raw and canned juice. Crowns were separated from the whole fruit and analysed separately.

The processing involved removal of the crowns and washing the remaining fruit, followed by removal of the tops and butts. The fruit were then peeled and cored and the peel, tops and butts cut up and dried to form one component of dried bran. The cores, shells and fruit pulp were disintegrated, leaving raw juice and pomace. The juice was heated to 93°C and canned; the pomace was dried and

added to the dried tops and butts to form dried bran. Crowns are normally used for re-planting, but occasionally may also be used as an animal feed item, as is pineapple foliage. Pineapple bran (wet and dry) is a major animal feed commodity.

When pineapple fruit were held in frozen storage (0-23°C) for 635-826 days the periods of degradation ranges were 4-24% for fenamiphos, 0-29% for fenamiphos sulfoxide and 0-4% for fenamiphos sulfone. The samples in the processing trial were stored for a maximum period of 218 days before analysis. The results are shown in Tables 99 and 100.

Table 99. Residues in Cayenne pineapples and their processed fractions, Hawaii, 1988 (Leslie, 1989a).

Application			PHI, days	Sample	Residues, mg/kg	Processing factor	Report no.
Form.	kg ai/ha	No.					
360 EC	16.79	7	14	whole fruit	0.67		99609 [1]
				raw crowns	8.32	12.4	
				dried bran	1.68	2.51	
				raw bran	1.44	2.15	
				canned juice	0.80	1.19	
				raw juice	0.40	0.60	

[1] 7 sprays applied at 14-34 day intervals at early flowering, post-flowering, fruit formation, fruiting, flat eye and maturing fruit stages. Plot size 7.9 m^2, silty clay soil, pH 2, 5% C. Limit of determination = 0.2 mg/kg. Recoveries of F, FSO and FSO_2 from fruit = 110, 67 and 75% at 0.2 mg/kg, 110, 76 and 93% at 0.4 mg/kg, 83, 70 and 71% at 1 mg/kg, and from raw crowns 90 and 73%, 89 and 74%, and 78 and 106% at 2 mg/kg, 86, 120 and 116% at 5 mg/kg, 106, 92 and 73% at 10 mg/kg.

The residues were higher in the pineapple crowns and bran than in the whole fruit, although in trials at rates corresponding to GAP the residues in the crowns and bran were not consistently higher than those found in the whole fruit.

Peanuts. Nemacur 15 GR was applied once to peanut crops, at a fivefold rate equivalent to 11.2 kg ai/ha (Leslie, 1989b). The band-over-row treatment was applied at the mid to late pegging stage, 60 days before final digging, by tractor-mounted equipment to a plot of 55.7 m^2. Inverted peanut plants were allowed to field-dry for 11 days before sampling threshed mature nuts in shell 71 days after treatment.

Processing involved drying and hulling to leave hulls, kernels and trash. The kernels were pressed to release the crude peanut oil, and the presscake yielded more crude oil by solvent extraction. The crude oil was separated into refined oil and soapstock, and the refined oil was hydrogenated and deodorised as for commercial use. The results are shown in Table 100.

Table 100. Residues in peanuts and their processed fractions, Georgia, USA, 1988 (Leslie, 1989b).

Application			PHI, days	Sample	Residues, mg/kg	Processing factor	Report no.
Form.	kg ai/ha	No.					
15 GR	11.2	1	71	kernels	0.01		99639 [1]
				meal	0.01	1	
				soapstock	<0.01	<1	
				crude oil	0.02	2	
				refined oil	<0.01	<1	

[1] Single band over row application at mid to late pegging. Plot size 55.7 m^2, sandy loam soil, pH 7, 0.7% C. Limit of determination = 0.01 mg/kg. Recoveries at 0.01, 0.02 and 0.05 mg/kg: fenamiphos 70-91% in kernels, 79-125% in meal, 78-99% in soapstock and 94-102% in crude oil; fenamiphos sulfoxide 82-110% in kernels, 72-106% in meal, 84-89% in soapstock and 77-114% in crude oil; fenamiphos sulfone 99-111% in kernels, 74-125% in meal, 77-84% in soapstock and 81-100% in crude oil.

Concentration of fenamiphos residues was only apparent in crude peanut oil, with no detectable residues in refined oil after treatment at an exaggerated rate.

Samples of peanut kernels were held in frozen storage (-23°C) for 223 days and the recovery of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone was measured. Fenamiphos sulfoxide levels showed a 3% reduction and there was no measurable loss of fenamiphos or fenamiphos sulfone. When vines were stored at -23°C for 155 days there was no apparent loss of fenamiphos.

Cotton. Nemacur 15 GR was applied at planting at an exaggerated rate of 14.45 kg ai/ha with band incorporation to a plot of 470.6 m^2 (Leslie, 1989c). Cotton bolls were harvested after 153 days at normal maturity. The bolls were ginned and the gin trash and lint separated from the cotton seed. The seed was delinted, hulled and processed into meal, soapstock, hulls, and crude and refined oil. The refined oil was further bleached, hydrogenated and deodorised for commercial use. The results are shown in Table 101.

Samples of cotton seed fortified with fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone at 0.1 mg/kg were held in frozen storage (–23°C) for up to 692 days. The average percentage decomposition after 687-692 days ranged from 19 to 26%. The samples in the processing trial were stored for a maximum period of 276 days before analysis.

Table 101**.** Residues in Delta Pine 50 cotton and its processed fractions, Mississippi, USA, 1988 (Leslie, 1989c).

Application			PHI, days	Sample	Residues, mg/kg	Processing factor	Reference
Form.	kg ai/ha	No.					
15 GR	14.45	1	153	cotton seed	0.01		Leslie 1989c[1]
				meal	<0.01	<1	
				soapstock	<0.01	<1	
				hulls	0.01	1	
				crude oil	0.02	2	
				refined oil	0.01	1	

[1] Plot size 471 m^2, sandy loam soil, pH 6, 1-2% C. Limit of determination = 0.01 mg/kg. Recoveries of F, FSO and FSO_2 at 0.01 mg/kg 98, 89%, 86, 108% and 97, 104% from seed; 102, 114%, 81, 111%, and 86; 89 and 90% from meal; 103, 108%, 90, 93, 106%, and 107 and 117% from hulls; 99%, 101% and 78% from soapstock; 67, 70, 71 and 82%, 110 and 76%, 77 and 77% from crude oil. Recoveries at 0.05 mg/kg were 71%, 90% and 103% from hulls, 82%, 73% and 84% from soapstock.

Residues were concentrated in crude oil, but reduced to their original level in the refining step.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

National monitoring data were reported by the governments of Australia and The Netherlands.

Table 102**.** Monitoring data for fenamiphos in The Netherlands (1994-1996).

Commodity	Samples	Samples below LOD (0.05 mg/kg)	Samples with residues <MRL	Samples with residues >MRL	Mean[1] mg/kg	MRL, mg/kg
Fruiting vegetables	390	389	–	1 (0.06)	<0.05	0.05*
Brassica vegetables	3306	3306	–	–	<0.05	0.05*
Leafy vegetables and fresh herbs	368	367	–	1 (1.4)	<0.05	0.05*

[1] For samples with residues below the LOD, half the LOD is taken for the calculation of the mean.

Table 103. Monitoring data for fenamiphos in Australia (Qld, 1996-1998 and NSW 1989-1997).

Commodity	No. of analyses	No. of samples with fenamiphos residues
Qld (1996-1998)		
Mandarins, oranges	7	0
Apricots, nectarines, peaches	16	0
Grapes	14	0
Carambola	1	0
Bananas, longans, mango, pawpaw, passion fruit	33	0
Eschallot	1	0
Broccoli, Brussels sprouts. cabbage, cauliflower, red cabbage, cabbage sugarloaf	22	0
Cucumber, rockmelon, zucchini	20	0
Chickpeas	2	0
Butter lettuce, Chinese cabbage, long Chinese cabbage, lettuce, silver beet	54	0
Capsicum, cherry tomato, chillies, egg plant, egg tomatoes, sweet corn, tomatoes	98	0
Carrot	6	0
Celery	1	0
NSW (1989-1997)		
Citrus	152	0
Apples, pears	253	0
Cherry, nectarine, peach	282	0
Strawberry, grapes, blueberry	292	0
Avocado, banana, kiwifruit, lychee, mango, pawpaw	361	0
Onion	178	0
Broccoli, cabbage, cauliflower	367	0
Cucumber (Lebanese), pumpkin, rockmelon, zucchini	330	0
Bok choy, Chinese cabbage, lettuce, lettuce (hydroponic), silver beet	463	1 (lettuce, <½ MRL)
Capsicum, mushroom, sweet corn, tomato	479	0
Beans	151	0
Carrot, potato	519	0
Asparagus, celery	159	0

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported. The residue is defined as “sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos”, unless otherwise stated.

Country	MRL, mg/kg	Commodity
Argentina	0.05	Kiwifruit, pineapple, sugar beet
	0.1	Banana, beans, coffee, coffee bean (roasted), cucumber, grapes, melon, pepper (sweet), potato, tobacco, tomato
	0.2	Grapefruit, onion, orange
Australia	0.005*	Milk
	0.05*	Banana, brassica vegetables, celery, citrus fruit, edible offal (mammalian), eggs, cucurbits, ginger, grapes, leafy vegetables (except lettuce), meat (mammalian), onion, peanut, pineapple, poultry (edible offal of), poultry meat, sugar cane
	0.1	Mushrooms,
	0.2	Lettuce (head), root and tuber vegetables, strawberry
	0.3	Lettuce (leaf)
	0.5	Tomato
	1	Aloe vera
Belgium [1]	0.05*	Other plant commodities
	0.1	Banana, coffee, grapes, potato
	0.5	Citrus fruit
Brazil [1]	0.1	Cacao, coffee, potato, tomato
Chile	0.05*	Carrot, sugar beet, citrus fruit (except orange), other fruit
	0.1	Grapes, orange pulp,
	0.2	Potato, tomato
Cyprus	0.05	Beets, melon, nuts, watermelon
	0.1	Citrus fruit (without peel), grapes

Country	MRL, mg/kg	Commodity
	0.2	Potato, tomato
	0.5	Banana, citrus fruit
Germany	0.05	Other plant commodities
	0.1	Banana, coffee, grapes
	0.2	Potato, tomato
Israel	0.05	Corn/maize, melon, onion, peanut, wheat
	0.1	Banana,
	0.2	Cucumber, potato, summer squash, tomato
Italy	0.05	Orange, peach, strawberry,
	0.1	Aubergine, bean (without pods), melon, onion, potato, sugar beet, tobacco, tomato
Malaysia	0.005	Milk, milk products
	0.05	Citrus fruit, cucumber, ginger, grapes, meat, onion, peanut, pineapple, tomato
	0.1	Banana, coffee, mushroom, pepper (black),sweet potato
Mexico	0.02	Asparagus, peanut
	0.05	Cotton seed, soya
	0.1	Banana, Brussels sprouts, cabbage, coffee
	0.2	Cacao, potato
	0.25	Apple, peach
	0.3	Okra, pineapple,
	0.5	Garlic
	0.6	Grapefruit, lemon, lime (sour), orange, tangerine
	1	Grapes
Netherlands	0.05*	Other plant commodities
	0.1	Banana, coffee, coffee (infusion), grapes, potato, sweet potato
	0.2	Orange
New Zealand	0.2	Root and tuber vegetables, tomato
Paraguay [1]	0.2	Tomato
Portugal	0.2	Potato
South Africa	0.05	Banana, citrus fruit, cotton seed, grapes, guava, litchi, nectarine, onion, papaya, pea (garden), peach, pecan nut (shelled),
	0.05 E	Grapes, nectarine, peach
	0.1	Ginger, pineapple, tomato
	0.2	Potato
	10	Tobacco
Spain	0.02	Berry (wild), brassica vegetables, cacao, cereals, coffee, cola, forage crops and straw, fruit and vegetables (dried), herbs, hops, leafy vegetables, mushrooms, nuts, oilseeds, other berries and small fruit, other bulb vegetables, other citrus fruit, other fruiting vegetables, other legume vegetables, other tropical/subtropical fruit, pome fruit, potato, pulses, root and tuber vegetables, rubus fruit, spices, stem vegetables, stone fruit, strawberry, sugar cane, sweet corn, tea, tobacco
	0.05	Cucumber, garlic, melon, sugar beet
	0.1	Banana, bean (pods and/or immature), grapes, pepper (sweet), tomato
	0.2	Orange
Switzerland	0.5	Orange
Turkey	0.01	Milk
	0.3	Citrus fruit
Uruguay [1]	0.2	Potato, tomato
USA [1]	0.02	Cacao, peanut,
	0.02 R	Asparagus [Connecticut, Delaware, Minnesota, Massachusetts, Maine, New Hampshire, New Jersey, New York, Pennsylvania, Rhode Island]
	0.05	Cotton seed, soya, cattle fat, cattle meat, cattle meat by-products, goat fat, goat meat, goat meat by-products, horse fat, horse meat, horse meat by-products, milk, pig fat, pig meat, pig meat by-products, sheep fat, sheep meat, sheep meat by-products
	0.1	Aubergine, banana, Brussels sprouts, cabbage, grapes, raspberry
	0.1 R	Kiwifruit [California]
	0.25	Apple, cherry, peach
	0.3	Okra, pineapple
	0.3 F	Grapes, raisins
	0.4	Peanut hulls
	0.5	Garlic
	0.5 R	Chinese cabbage [California]
	0.6	Citrus fruit, strawberry

Country	MRL, mg/kg	Commodity
	0.6 R	Peppers (non-bell) [Georgia, Puerto Rico, California]
	1 R	Garden beet tops [New York, Pennsylvania, Illinois, Indiana, Michigan, Ohio]
	1 F	Grape pomace
	1.5 R	Garden beet root [New York, Pennsylvania, Illinois, Indiana, Michigan, Ohio]
	2.5	Citrus fruit molasses
	2.5 F	Citrus fruit pulp (dry)
	10	Pineapple bran
	25 F	Citrus fruit oil, refined

[1] Residue defined as sum of fenamiphos, its sulfoxide and sulfone.
E = export tolerance. F = Food additive tolerance. R = Regional tolerance.

APPRAISAL

Fenamiphos was first reviewed by the JMPR in 1974, with subsequent residues evaluations in 1977, 1978 and 1980. The compound was scheduled for periodic review at the 27th Session of the CCPR (ALINORM 95/24A Appendix IV). At the 30th (1998) Session it was noted that the TMDI based on existing CXLs slightly exceeded the revised ADI of 0.0008 mg/kg body weight allocated by the 1997 Meeting.

The manufacturer submitted a comprehensive data package in support of the existing CXLs for bananas, Brussels sprouts, cabbages, coffee beans, cotton seed, grapes, melons, oranges, peanuts, pineapples and tomatoes. Additional data were reported to estimate new maximum residue levels for apples, cherries, lemons, limes, grapefruit, onions, peaches and peppers.

Physicochemical data for fenamiphos indicate that the compound is moderately soluble in organic solvents (10-20 g/l) and highly soluble in toluene and 2-propanol (>200 g/l at 20° C).

Animal metabolism

The metabolism of fenamiphos was investigated in rats, a lactating goat, a dairy cow and laying hens.

In a series of four experiments, rats were dosed with [*phenyl*-1-^{13,14}C]fenamiphos as a single low i.v. dose, a single low oral dose, repeated low oral doses and a single oral dose at 10 times the low dose rate. Similar patterns of elimination and transformation were observed in all cases. Urine was the main route of elimination, with 93-100% of the radioactivity recovered within 48 hours after administration. In the faeces 1.5-3.8% of the dose was eliminated during the first 48 hours. The total radioactivity in the tissues, including the GI tract, was 0.045-0.23% of the administered dose; the radioactivity in the tissues of all the animals was below the limit of quantification and was not examined further.

The identified radioactivity in the excreta accounted for more than 93% of the total recovered radioactivity. The main metabolites in the urine and faeces were fenamiphos sulfoxide phenol (FSOP) accounting for 4-22% and its sulfate conjugate (FSOP-sulfate), 40-54%. The presence of these compounds indicates that a major transformation pathway in rats involves oxidation of the methylthio group, with cleavage of the isopropyl chain on the amine and of the phosphate ester function.

The most recent toxicological review of fenamiphos by the JMPR was in 1997. The findings in the rat studies were identical, *i.e.* fenamiphos was rapidly excreted, with >96% of the radioactivity excreted renally by 48 hours after dosing. At 48 hours, most of the residues in the tissues were below the limits of quantification. The main urinary metabolites were fenamiphos sulfoxide phenol sulfate, fenamiphos sulfoxide phenol, fenamiphos phenol sulfate and fenamiphos sulfone phenol sulfate.

In a dairy cow study, [U-*phenyl*-^{14}C]fenamiphos sulfoxide was administered in a single dose of 0.8 mg/kg body weight. Blood, milk and urine samples were taken at hourly intervals and faeces were collected upon elimination. Four hours after administration, the animal was slaughtered and tissue samples including GI tract were taken for analysis. Approximately 88% of the administered dose was recovered, with 47% in the rumen contents, 39% in the urine, and 1.4% in the tissues.

Peak radioactivity in the blood of 0.24 mg/kg fenamiphos sulfoxide equivalents was observed 1 hour after dosing, with a steady decrease to 0.09 mg/kg 4 hours after administration. The main source of the recovered radioactivity in the blood was fenamiphos sulfoxide phenol at levels of 55 to 74%.

The radioactivity in the milk peaked in the 4 hour samples at a level of 0.061 mg/kg fenamiphos sulfoxide equivalents. The predominant radioactive components were fenamiphos sulfoxide phenol (37-40%) and fenamiphos phenol (<21%); 27-46% of the radioactivity remained unidentified.

In the urine, fenamiphos sulfoxide phenol was the main component of the total radioactive residue, at levels of 60-70% of the recovered radioactivity over the 4-hour period of the study.

Metabolites were identified in specific tissue samples, including muscle, fat, liver, kidney and heart. A large proportion of the radioactivity remained unidentified. Of the identified compounds, unchanged fenamiphos sulfoxide and fenamiphos sulfoxide phenol were the predominant compounds; fenamiphos was detected in the liver, fat, kidneys and heart.

[*Phenyl*-^{14}C]fenamiphos was administered to a lactating goat at a dose of 1 mg/kg body weight for 3 days. Samples of blood, urine, faeces and milk were taken at regular intervals. Peak plasma radioactivity equivalent to 0.6 μg/ml was observed 0.25 hours after the first dose and decreased steadily to 0.12 μg/ml at 6 hours after administration. A half-life of 4.5 hours was calculated for the elimination of the radioactivity from plasma during the 1-6 hours after administration of the first dose.

The total recovered radioactivity was 65.5%, with urine accounting for 61% of the dose. Additional elimination in the faeces and milk accounted for 3.6% and 0.06% of the dose respectively. Radioactivity in edible tissues and organs totalled 0.3% of the dose.

The main radioactive metabolites in milk were fenamiphos phenol sulfate, fenamiphos sulfoxide phenol sulfate and fenamiphos sulfone phenol sulfate. Conjugate formation increases the water-solubility of the metabolites, so similar metabolite patterns are found in urine and in milk.

In edible tissues, the highest radioactivity was present in the liver and kidneys, at levels of 0.13 and 0.04 mg/kg fenamiphos equivalents respectively, or 0.09 and 0.04% of the recovered radioactivity. The main radioactive components in liver were fenamiphos sulfoxide and fenamiphos sulfoxide phenol. In kidney however, the main metabolites were fenamiphos sulfoxide phenol sulfate and fenamiphos sulfone phenol sulfate, again indicating that conjugation is a necessary transformation before the elimination of the metabolites. The tissues were re-analysed 8 and 24 months after the initial extractions. At 8 months similar results were found in both liver and kidney, but re-analysis of the liver samples at 24 months showed that the metabolites initially present had undergone some reductive transformation to fenamiphos and fenamiphos phenol sulfate.

Three types of muscle samples were analysed for metabolite composition: loin, flank and round. In round and loin muscle, the compounds present were fenamiphos sulfoxide, fenamiphos sulfoxide phenol sulfate and fenamiphos sulfone phenol sulfate. In flank muscle however, they were desisopropyl-fenamiphos sulfone, fenamiphos sulfoxide phenol and fenamiphos sulfone phenol sulfate, indicating incomplete transformation from fenamiphos sulfoxide to fenamiphos sulfoxide

phenol sulfate in flank muscle, as cleavage of the isopropyl and phosphate ester groups are two of the main processes of metabolic degradation of fenamiphos.

Laying hens were dosed orally with [*phenyl*-1-^{13,14}C]fenamiphos at 1 mg/kg body weight for 3 days. Blood, excreta and eggs were collected at regular intervals. The birds were killed 0.5 hours after the third dose.

Peak radioactive levels of 0.44 μg/ml were found in plasma 0.5 hours after the third dose, and decreased to 0.03 μg/ml at 24 hours. An elimination half-life of 4.3 hours was calculated from samples taken over a 24-hour period after administration. The total recovered radioactivity in individual birds ranged from 64 to 73% of the administered dose with excreta contributing to 60-70% of the total radioactivity. The TRR in eggs amounted to 0.03% and in tissues from 1.74 to 4.85%. The highest levels of radioactivity, 0.23, 0.61 and 2.2 μg/g fenamiphos equivalents, were present in the kidneys, liver and gizzard respectively.

The predominant metabolites in the tissues and eggs were fenamiphos phenol, fenamiphos sulfoxide phenol, fenamiphos sulfone phenol and/or their sulfate conjugates. Unchanged fenamiphos was also present in all tissues and eggs. The main pathways of transformation in hens include oxidation of the methylthio group and cleavage of the phosphate ester group, followed by conjugation of the resulting phenols.

In summary, the primary processes of metabolism in rats, goats, cows and hens involve oxidation of the methylthio sulfur, cleavage of the isopropyl group leaving a primary amine, cleavage of the phosphate ester group and conjugation of the resulting phenols leading to ease of elimination. Evidence of cleavage of the isopropyl group was found only in the goat and hen studies, where desisopropyl-fenamiphos sulfoxide was identified as an additional metabolite.

Plant metabolism

Studies on beans, tomatoes, carrots, cabbage and pineapples were reported. Application methods included spray, stem injection, soil treatment and uptake from solution. Snap beans were treated with [*ethyl*-^{14}C] and [*methylthio*-^{3}H]fenamiphos by stem injection (1 mg/plant) or soil treatment (6.7 kg ai/ha). After 4 weeks the plants were sampled and extracted. After soil treatment most of the radioactivity was recovered from the soil, with the remainder present in plant solids and as volatiles caught in acid and base traps. Less than 1% of the applied ^{14}C was present in extracted plant material. After stem injection most of the radioactivity was trapped as volatile compounds or remained as unextracted plant material; 11% of the applied ^{14}C was extracted. The main extractable ^{14}C metabolites from both treatments were fenamiphos sulfoxide and fenamiphos sulfone.

In a subsequent study bean plants were treated by uptake from solution and stem injection. Uptake from solution resulted in a slower incorporation of the radiolabel into the plants, so the predominant extracted radioactive compound was parent fenamiphos instead of fenamiphos sulfoxide during the first 14 days.

[*Ethyl*-^{14}C] and [U-*phenyl*-^{14}C]fenamiphos were applied as soil treatments to tomatoes at a rate equivalent to 6.7 kg ai/ha, 20-30 days before fruit maturity. The distribution of radioactivity in the fruit was investigated up to 74 days after treatment. Most of the radioactivity was extracted, with less than 3% of the ^{14}C present in insoluble fractions from the ring label but up to 36% from the ethyl label. This difference is presumably because different fragments of fenamiphos are incorporated after cleavage into plant components. The predominant radioactive components of the residue in the organic extracts were fenamiphos sulfoxide and fenamiphos sulfone, confirming that oxidation of the methylthio group followed by cleavage of the phosphate ester function are the main transformation pathways in plant metabolism.

Carrots were transplanted into soil treated with [*ethyl*-^{14}C]fenamiphos at a rate equivalent to 10 kg ai/ha. Whole plants were harvested 53, 67 and 86 days after treatment. A large proportion of the radioactivity in both roots and foliage (34-66%) was present in unextracted solids and similar proportions of the radioactivity were extracted into aqueous and organic phases. Hydrolysis of the aqueous extracts showed that most of the water-soluble radioactivity was due to the phenol sulfoxide and phenol sulfone conjugates.

[*Ethyl*-^{14}C] or [U-*phenyl*-^{14}C]fenamiphos was applied as a soil treatment at a rate equivalent to 13.4 or 33.6 kg ai/ha before transplanting cabbage seedlings. Cabbage heads were harvested at intervals up to 90 days after treatment and samples of whole head, outer and inner leaves were analysed for radioactivity. The results indicated that as the crop matures the aqueous extractable radioactivity increases and the organic extractable radioactivity decreases. The total radioactivity and its distribution in outer and inner leaves after treatment with [*ethyl*-^{14}C]fenamiphos were similar at the same sampling intervals. The main identified radioactive components in the organic extractable fractions were generally fenamiphos sulfoxide and fenamiphos sulfone. Enzymic hydrolysis of the aqueous fractions indicated that the water-soluble metabolites were glucoside conjugates of phenol derivatives of fenamiphos. Acid digestion of the insoluble fraction yielded the metabolites found in the organic phase, *i.e.* fenamiphos sulfoxide and fenamiphos sulfone.

In a series of five experiments, pineapple plants were treated with [*ethyl*-^{14}C] or [U-*phenyl*-^{14}C]fenamiphos either as a soil treatment, spray or stem injection. Most of the radiolabel from the soil treatment was present in the soil, with a gradual increase in the radioactivity in the pineapple foliage up to 90 days after treatment. As in cabbages and carrots, there was an increase in the radioactivity in the aqueous and insoluble fractions with time compared to the proportion of organosoluble radioactivity, irrespective of the application method. The predominant radioactive components were fenamiphos sulfoxide and sulfone, with lower levels of the corresponding phenols. Similar metabolite patterns were observed after spray treatment and stem injection. Enzymatic hydrolysis of the aqueous fractions yielded 14-34% of the applied radioactivity as fenamiphos sulfoxide phenol and 6-14% as fenamiphos sulfone phenol after stem injections and spray applications.

Crop rotation studies were conducted with various crops including cereals, a root crop, an oilseed crop and leafy vegetables after treatment of the soil at 7.6 kg ai/ha. The results with the different crops were similar and in agreement with the plant metabolism studies, *i.e.* the radioactivity extracted into aqueous fractions and remaining in the plant solids increased with time owing to conjugation of fenamiphos sulfoxide and sulfone phenols. The soil radioactivity was measured at each cropping interval and the patterns of degradation observed in the soil and rotational crops were similar.

The maximum residues of fenamiphos sulfoxide and fenamiphos sulfone (as fenamiphos equivalents) were 0.08-6.55 mg/kg and 0.04-5.41 mg/kg respectively in the crops and crop fractions investigated after the first rotation (30 days). In the second rotation (120 days), fenamiphos sulfoxide and fenamiphos sulfone residues ranged from 0.02 to 2.82 mg/kg and 0.01 to 2.90 mg/kg respectively, and in the third rotation (269 days) the corresponding residues were <0.01-0.39 mg/kg and <0.01-0.62 mg/kg.

The additional metabolites desisopropyl-fenamiphos sulfoxide and desamino-fenamiphos sulfoxide were both identified in the rotational studies and provide evidence that cleavage of the isopropyl group and the resulting amino group are among the metabolic transformations that occur in plants.

In another crop rotation study, unlabelled fenamiphos was applied to the soil at a rate equivalent to 6.72 kg ai/ha and incorporated after application. Rotational crops of wheat, sorghum, turnips, spinach and mustard greens were planted 1, 4 and 8 months after the soil treatment. Soil samples were taken immediately after treatment and at planting and harvest of the rotational crops. The residues were <0.01 mg/kg at 4 months plant back in all samples except spinach leaves and

sorghum forage and straw. The residues in sorghum forage were 0.44 and 0.68 mg/kg and in straw 0.02 mg/kg at one site, but <0.01 mg/kg at another site. After 8 months plant back the residues were <0.01 mg/kg in all sorghum plant fractions. The residues in spinach leaves were 0.03 mg/kg at 4 months plant back.

In summary, the conclusions from the plant metabolism studies were that fenamiphos sulfoxide and fenamiphos sulfone are the main metabolites formed after the application of fenamiphos by various methods. In crops with a substantial period from treatment to harvest fenamiphos sulfoxide phenol and fenamiphos sulfone phenol are also formed, as is apparent by the change in the extraction characteristics of the radioactivity with time. Overall, the metabolites of fenamiphos in plants and animals are similar and the existing definition of the residue as "sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos" is appropriate.

Environmental fate

The photodegradation of [U-*phenyl*-^{14}C]fenamiphos on soil proceeds via first order kinetics with measured half-life values of 1.6 hours under laboratory conditions (Hg vapour lamp) and 2.7 hours in natural sunlight. The main photolytic products are fenamiphos sulfoxide and fenamiphos sulfone.

The adsorption/desorption properties of fenamiphos were investigated in four types of soil ranging from sand to clay loam. Measured K_{oc} values for fenamiphos indicated low mobility in the sandy soil and medium mobility in sandy loam, silt loam and clay loam (K_{oc} 150-500 medium mobility; 500-2000 low mobility). In another study, the adsorption / desorption characteristics of fenamiphos were investigated in 16 soils from different geographic locations, ranging from cool/moderate to sub-tropical climates. The highest adsorption capacity was measured in a soil with high clay and silt contents. In all the soils higher adsorption constants were found for fenamiphos than for fenamiphos sulfoxide phenol or fenamiphos sulfone phenol. Silt loam adsorbed a higher proportion than clay loam of both fenamiphos sulfoxide and fenamiphos sulfone.

Degradation half-lives of $\leq$30 days were reported for fenamiphos in aerobic conditions, with fenamiphos sulfoxide and fenamiphos sulfone the main degradation products. The half-life in anaerobic conditions was 87.9 days, with fenamiphos sulfoxide the main degradation product. In aerobic soil degradation studies conducted in 16 soils from different geographic locations, half-lives were reported as less than 15 days at 22º C. In an outdoor degradation study, the half-life of fenamiphos was reported as 19.9 and 18.2 days in predominantly sandy soils at two sites in California.

In leaching experiments with aged residues, [^{14}C]fenamiphos was applied to soil and the mixture aged for 63 days. The treated soil was applied to columns containing a sandy loam and a silt loam, which were eluted for 48 hours with water. Less than 1% of the applied radioactivity was found in the eluates; up to 16% was collected as volatiles. Fenamiphos was mainly converted to fenamiphos sulfoxide in the aged soil.

In two field dissipation studies degradation half-lives of 15 and of 15.9 days were reported for fenamiphos. Soil core samples were taken after 1 and 2 sprays of fenamiphos at 12.3 kg ai/ha. The maximum residues of fenamiphos were 1.5 and 2.7 mg/kg and 2.0 and 2.5 mg/kg after the 1st and 2nd sprays respectively, and of fenamiphos sulfoxide 3.3 and 4.1 mg/kg after the first applications and 2.0 and 2.5 mg/kg after the second; they decreased to <0.01 mg/kg at 90, 93 and 254, 361 days after the 1st and 2nd sprays, at all soil depths examined (down to 61 cm). The results indicate that fenamiphos is degraded rapidly, whereas fenamiphos sulfoxide dissipates at a relatively rapid rate after 1 spray and more slowly after 2 sprays.

Calculated half-lives for the hydrolysis of fenamiphos in buffer solutions at pH 3 and 9 were 3-10 and 22-230 days respectively. In pH 3 buffer solution, the main hydrolysis product was deaminated fenamiphos, with fenamiphos phenol and deaminated fenamiphos phenol present below 10% of the applied concentration. At pH 9 however, the main hydrolysis products were fenamiphos

phenol, fenamiphos sulfoxide phenol and fenamiphos sulfoxide, presumably owing to base hydrolysis of the phosphate ester group. At elevated temperatures of 60, 70 and 80° C the half-lives ranged from 1.7-9.8 days, 14-67 days and 5-70 hours at pH 4, 7 and 9 respectively.

In sterile solutions at pH 5, 7 and 9 which were kept in the dark, the calculated half-lives for hydrolysis ranged from 235-301 days, with the longest at pH 7.

Aqueous solutions of fenamiphos in phosphate buffer were irradiated under laboratory conditions (Hg lamp) and samples were analysed at regular intervals up to 24 hours. The half-life was calculated as 3.6 hours and the main photolytic products at 24 hours were fenamiphos sulfoxide and fenamiphos sulfonic acid phenol.

In summary, the degradation of fenamiphos in soil and water proceeds via oxidation of fenamiphos to fenamiphos sulfoxide and fenamiphos sulfone, so the products formed are similar to the metabolites formed in plants and animals. An additional product detected was fenamiphos phenol sulfonic acid, formed by oxidative demethylation of the methylthio group and hydrolysis of the phosphate ester.

Methods of residue analysis

Analytical methods for the determination of fenamiphos and its metabolites in various plant substrates, animal tissues, soil and water are based on the published method of Thornton (1971). The method was originally validated for citrus peel and pulp, pineapple fruit, bran and forage, peanut kernels, hulls and vines, and tobacco. Several modifications were subsequently reported. The basic procedure involves homogenization of the sample, filtering, and partitioning the solution with methyl chloride or other organic solvents. The organic extract is evaporated to dryness, and the residue is redissolved in acetone and oxidised with $KMnO_4$ solution. The oxidised residues are partitioned again into methyl chloride, which is evaporated before dissolution in acetone for quantification by GLC with an FPD in the phosphorus mode. Total residues of fenamiphos, fenamiphos sulfoxide and fenamiphos sulfone are quantified in a single sulfone peak. The limits of determination in various crops are reported as 0.01-0.1 mg/kg

Fenamiphos is included in multi-residue enforcement methods which were provided by the governments of Australia and The Netherlands. In the *Official Methods of Analysis in The Netherlands*, fenamiphos is quantified at a limit of 0.05 mg/kg in various crops; recoveries were reported for lettuce. In fatty foods the limit of determination is also 0.05 mg/kg. Inclusion of the sulfoxide and sulfone metabolites was not mentioned. Fenamiphos is quantified at a limit of 0.02 mg/kg in crops in the method provided by the Australian government.

Analyses of animal tissues involve quantification of total residues including fenamiphos sulfoxide, sulfone and sulfoxide phenol (FSO, FSO_2, and FSOP). The metabolites desisopropyl-fenamiphos and its sulfoxide and sulfone (DIF, DIFSO and $DIFSO_2$) are quantified in an additional peak containing the methylated residues. The work-up procedures for animal tissues and milk are similar to those for crops, but CH_3CN is used in the partitioning steps before oxidation. Reported limits of quantification in milk and tissues are 0.005 and 0.01 mg/kg respectively.

The limits of quantification in soil and water are 0.01 mg/kg and 0.1 µg/l respectively. An electrospray MS method was developed for the determination of fenamiphos and its degradation products in soil. Deuterated fenamiphos is introduced into the soil sample as an internal standard before work-up, followed by extraction in CH_3CN and analysis by LC-MS-MS. Aliquots are then analysed by HPLC/MS to determine fenamiphos and its sulfoxide and sulfone. The limit of determination for the individual compounds is 0.01 mg/kg.

Recoveries were determined by fortification with fenamiphos alone or a mixture of fenamiphos and its sulfoxide and sulfone.

The stability of residues was determined in stored samples of a number of crops including asparagus, banana, cotton seed (seed, meal, hulls and oil), garlic, and grapes (berries, juice, wet and dry pomace and raisins). Samples were fortified with a mixed standard composed of fenamiphos, FSO and FSO_2 at 1 mg/kg each (3 mg/kg total) and held in frozen storage (≤-5° C) for up to 18 months. Some decrease of total residues (<10%) was observed in garlic and grape pomace after 12 months. At 18 months <10% decrease was found in most commodities and crop fractions except raisins and cotton seed hulls, which had decreased by <20%. The Meeting agreed that a decrease of <20% should not be considered significant, and that residues in the commodities examined were stable when stored frozen for 18 months.

In a study of the storage stability of residues in animal tissues, extracts of cattle fat, kidney, liver and muscle were fortified separately with 1 mg/kg fenamiphos, DIF, FSO, DIFSO, FSO_2 or $DIFSO_2$, and milk with 1 mg/kg fenamiphos, FSO or FSO_2. Tissues and milk were stored at -25° C for up to 2 and 3 months respectively. The results showed that fenamiphos, FSO and FSO_2 were stable in milk for 61 days, but fenamiphos was unstable in fat, liver, kidney and muscle, and was degraded within 83 days. As fenamiphos would have been converted to its sulfoxide and sulfone and the analytical method determines total residues as fenamiphos sulfone, the total fenamiphos residues in tissues are considered to be stable.

Use pattern

Fenamiphos is registered in many countries as a nematicide. Numerous labels from registered products were submitted by the manufacturer. For many crop uses, fenamiphos is applied pre- or post-planting as a soil treatment, in-furrow spray or by drip irrigation. To established crops, it is applied as a spray to individual plants or trees, with repeat treatments if necessary. Both fenamiphos sulfoxide and fenamiphos sulfone also exhibit nematicidal activity.

Supervised trials

Data were provided in support of the existing CXLs for bananas, Brussels sprouts, cabbages, carrots, coffee beans, cotton seed, grapes, melons, pineapples, potatoes and tomatoes. New data were reported on apples, cherries, lemons, limes, grapefruit, onions, peaches, peppers and zucchini.

The residues in the supervised crop trials were determined as the sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos.

Root, tuber and bulb vegetables. There are existing CXLs for fenamiphos in carrots, potatoes and sweet potatoes.

Trials on carrots were conducted in Australia, Italy and Spain. Fenamiphos was applied to soil before sowing in all the trials. The registered use pattern in Australia is for a single application at a maximum rate of 9-9.6 kg ai/ha and a PHI of 84 days. In Italy, a single application of 15 kg ai/ha is registered with a PHI of 90 days. The Spanish trials were not directly comparable to a registered use in Spain and were evaluated against GAP in Italy. Where higher rates of application gave residues below the limit of detection the results were also used in the estimation of the maximum residue level. The residues from trials according to GAP ranged from <0.02 to 0.08 mg/kg. The residues in rank order were <0.02 (8), 0.02, 0.024, 0.027, 0.05, 0.06 (2), 0.07 and 0.08 mg/kg. The Meeting estimated a maximum residue level of 0.2 mg/kg (the existing CXL) and an STMR of 0.02 mg/kg. (HR = 0.08 mg/kg).

Supervised trials on potatoes were conducted in Australia and Spain. Registered uses in Australia allow single applications at a maximum rate of 10 kg ai/ha with a PHI of 84 days. In Spain single applications of 8-10 kg ai/ha are allowed with a PHI of 120 days. The treatments were applied pre-planting. The residues in the tubers were <0.01-0.17 mg/kg in six trials. The Meeting considered

that there were insufficient data to confirm the existing CXL of 0.2 mg/kg and recommended its withdrawal.

As no data were provided for sweet potatoes, the Meeting recommended withdrawal of the existing CXL of 0.1 mg/kg.

Trials on onions were conducted in Australia and South Africa. The product was applied to soil 4 or 5 days before sowing. The registered use in Australia is for a single application at 9.7 kg ai/ha with a PHI of 84 days. In South Africa the maximum rate is 3 kg ai/ha with a PHI of 80 days. Some samples in one of the South African trials were not fully mature although the reported PHIs in that trial were longer than in the other trials. The residues in onion bulbs ranged from <0.01 to 0.05 mg/kg in trials which complied with GAP. The Meeting considered that there were insufficient data to estimate a maximum residue level.

Brassica vegetables. There are existing CXLs for broccoli, Brussels sprouts, cabbages and cauliflower.

Data from 7 trials in the USA were provided for Brussels sprouts. The registered use pattern allows single applications of 6.7 kg ai/ha at planting with no specified PHI. The residues in 6 trials were <0.01 mg/kg; in the other trial a higher rate of 10 kg ai/ha was employed which resulted in residues of 0.02 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg, and recommended the withdrawal of the existing CXL of 0.05* mg/kg (HR = 0.01 mg/kg).

Trials on cabbages were conducted in Australia and the USA. The registered use pattern in Australia for crucifers is a single application up to 7 days before planting at a rate of 9-11 kg ai/ha and no specified PHI. GAP in the USA allows single applications at 6.7 kg ai/ha with no specified PHI. The residues in cabbage heads were <0.01-0.05 mg/kg in 12 US trials which complied with GAP. The residues in all the trials according to GAP in rank order were <0.01 (10), 0.01, <0.02, 0.02 (3) and 0.05 mg/kg. The Meeting recommended the withdrawal of the existing CXL of 0.05* mg/kg and estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg (HR = 0.05 mg/kg).

In the US trials, wrapper leaves and field trash were also analysed for fenamiphos residues. The residues in the wrapper leaves were slightly higher than those levels found in the cabbage heads.

No data in support of the existing CXLs for broccoli and cauliflower were submitted. No information on specific GAP for cauliflower or broccoli was provided, although there are registered uses for brassicas in Costa Rica and crucifers in Australia. The Meeting agreed to recommend withdrawal of the existing CXLs for broccoli and cauliflower.

Fruiting vegetables. Supervised trials on peppers were conducted in Italy, Spain and Portugal in glasshouses and under field conditions. Applications ranged from several days before planting in the field trials to drip irrigation at flowering or early stages of fruiting in the glasshouse trials. Data from trials with an encapsulated formulation (CS) have been recorded in the Tables, but registration of the product is only pending in Spain and Portugal and the data were therefore not used in the estimation of the maximum residue level and STMR. Current registered uses in Spain are single applications at planting at rates of 5-10 kg ai/ha with a PHI of 90 days.

The residues in peppers ranged from <0.02 to 0.35 mg/kg after treatment with GR and EC formulations, and from <0.02 to 0.31 mg/kg after treatment with the CS formulation. The range of residues was similar from treatment with the registered formulations and the CS product. The residues in rank order were <0.02, <0.05, 0.05 (2), 0.06 (2), 0.26 and 0.35 mg/kg. A maximum residue level of 0.5 mg/kg and an STMR of 0.055 mg/kg were estimated. (HR = 0.35 mg/kg).

Sixteen field and 11 glasshouse trials on tomatoes were conducted in Australia, Brazil, Italy, Portugal, South Africa and Spain with GR, EC, EW and CS formulations. In the field trials fenamiphos was applied at or shortly after planting, and in the glasshouse trials application was by drip irrigation pre-flowering or at early fruit formation. The registered use in Australia is for single applications at a maximum rate of 11 kg ai/ha with no specified PHI. In Brazil a single application at 3-4 kg ai/ha with a PHI of 90 days is registered. The Italian use pattern is for single applications at 10-15 kg ai/ha with a PHI of 20 days. In Portugal, a maximum of 3.4 kg ai/ha may be applied in a single treatment with a PHI of 20 days. On South African labels, application rates are expressed in g ai/m, allowing a maximum of 1 g ai/m and unspecified PHI. Spanish labels for the GR and EC products specify single applications at rates of 5-10 kg ai/ha with a PHI of 90 days.

The residues in tomatoes were <0.02-0.30 mg/kg after treatment with the GR and EC formulations and <0.02-0.15 mg/kg after treatment with the CS formulation. Although the CS product is a pending registration, the residues from the CS trials were within the range found for the currently registered formulations. The residues from the CS formulation were not considered in the estimation of the maximum residue level or STMR. The residues in rank order were <0.02 (4), <0.05 (5), <0.1, 0.15, 0.17, 0.27 and 0.30 mg/kg. The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.05 mg/kg, and recommended withdrawal of the existing CXL of 0.2 mg/kg (HR = 0.30 mg/kg).

Four glasshouse trials on zucchini were conducted in Italy in which the CS formulation was applied at the 3 to 5 leaf stage of growth. The proposed GAP for the CS product in Spain allows single applications at 10 kg ai/ha with a PHI of 90 days. The residues were <0.02 mg/kg in all the trials. As registration of the CS product is pending and there were no trials with registered formulations, a maximum residue level for zucchini could not be estimated.

Thirteen field and 9 glasshouse trials on melons were conducted in Australia, Brazil, Guatemala, Mexico and Italy with GR, EC and CS formulations. Application timings ranged from 14 days before sowing to flowering. In many trials residues were determined in the whole fruit and pulp; in some the residues in peel were reported separately. Registered use patterns in Australia are for single applications at a maximum rate of 9.6 kg ai/ha and no specified PHI. In Brazil, labels recommend single applications at 4 kg ai/ha with no specified PHI. The 10, 12 and 15 GR products are registered in Guatemala with single applications at a maximum rate of 5.1 kg ai/ha and a PHI of 60 days. In Italy the 5 GR product may be applied at rates of 5-10 kg ai/ha with a PHI of 20 days. In Spain GR and EC products are registered with a maximum rate of 10 kg ai/ha and a PHI of 90 days. Registration of the CS formulation is pending. The trials in Mexico were evaluated against the registered uses in Guatemala.

The residues in the whole fruit after treatment with the GR and EC formulations were <0.01-<0.05 mg/kg. In trials with the CS formulation residues in the whole fruit were <0.02-0.03 mg/kg. The residues in the pulp were below the reported limit of detection or determination in all the trials. The residues in the whole fruit in rank order were <0.01 (6), <0.02 (3) and <0.05 (4) mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg, the same as the existing CXL. The residues in the pulp in rank order were <0.01 (4) and <0.02 mg/kg. The Meeting estimated an STMR of 0.02 mg/kg for melon pulp (HR = 0.02 mg/kg).

Two trials on watermelons were carried out in Italy, where the registered use pattern is a single application of a GR product at 5-10 kg ai/ha with a PHI of 20 days. Sampling in the trials was at fruit maturity, 85-109 days after treatment, so the PHI was not observed although the application was made up to 20 days before planting. The residues in the whole fruit and pulp were below the limit of determination of 0.02 mg/kg. The Meeting agreed that as there were few trials for watermelons and Italian GAP for melons and watermelons is identical, the trials on melons could be used to support a recommended MRL for watermelon. A maximum residue level of 0.05* mg/kg was therefore estimated for watermelon, with an STMR of 0.02 mg/kg (HR = 0.02 mg/kg).

Citrus fruits. Many of the trials on citrus fruit were conducted in the USA at excessive treatment rates. In trials on grapefruit, lemons, limes and oranges, soil applications were made at rates of 2.4 and 4 times the registered label rates. The registered use patterns for citrus fruits in the USA prescribe single applications at a maximum rate of 8.4 kg ai/ha with a PHI of 30 days. In many trials, residues were reported in the whole fruit, pulp and peel.

Supervised trials on grapefruit in the USA were at rates equivalent to 4 times the maximum label rate. The residues were <0.01-0.29 mg/kg and <0.01-0.08 mg/kg in the whole fruit and pulp respectively, in samples taken at PHIs of 30-243 days. As the trials did not reflect GAP in the USA and application at excessive rates resulted in detectable residues, the data could not be used to estimate a maximum residue level for grapefruit.

Seven trials on lemons were conducted in Australia, South Africa and the USA. Again in the 5 US trials, the rates were equivalent to 2.6 or 4 times the maximum registered rate. The registered use pattern in Australia is single applications at 30 kg ai/ha with no specified PHI. In South Africa, GAP allows a maximum rate of 12 kg ai/ha or 2 g ai/m^2 to be applied with a PHI of 150 days. The residues from the Australian and South African trials were <0.05 mg/kg in the whole fruit, pulp and peel. The residues in the US trials were <0.01-0.44 mg/kg in the whole fruit and <0.01 mg/kg in the pulp. The Meeting considered that 5 of the 7 trials were not according to GAP and could not be used to estimate a maximum residue level for lemons.

In two US trials on limes the rates of application were 4 times the maximum GAP rate. The residues in the whole fruit 147 days after treatment were below the limit of detection of 0.01 mg/kg.

Trials were conducted in Australia, South Africa and the USA in support of the existing CXL of 0.5 mg/kg for oranges. All the trials in the USA were at rates of 2.6 or 4 times the maximum registered rate. GAP in Australia and South Africa is identical to that for lemons. The residues in the whole fruit were <0.02-0.08 mg/kg in the trials in Australia and South Africa. In the US trials the residues were <0.01-0.17 mg/kg in the whole fruit and <0.01-0.02 mg/kg in the pulp. As most of the trials were in the USA at excessive rates they could not be used to estimate a maximum residue level. The Meeting therefore recommended the withdrawal of the existing CXL for oranges.

In summary, the Meeting concluded that as exaggerated treatments were applied in most of the trials on citrus fruits and residues above the limit of determination were found at varying intervals after treatment, no maximum residue levels could be estimated.

Pome fruits. Numerous trials on apples were conducted in the USA where the registered use rates are 5.4-8.2 kg ai/ha with a PHI of 72 days. The trials were all at a rate of 22.4 kg ai/ha, 2.6 times the maximum rate. The residues in the whole fruit in all 33 trials were below the limit of detection of 0.01 mg/kg; the reported limit of determination was 0.05 mg/kg. Although the trials were not in accord with US GAP, the Meeting considered that as there were no detectable residues in any of the trials after exaggerated treatments, the data could be used to estimate a maximum residue level of 0.05* mg/kg and an STMR of 0.01 mg/kg (HR = 0.01 mg/kg).

Stone fruits. Nineteen supervised trials on cherries were conducted in the USA, 16 at 2.7 and 3 at 1.7 times the maximum registered rate (8.2 kg ai/ha with a PHI of 45 days). The residues in the whole fruit ranged from <0.01 to 0.18 mg/kg at PHIs of 45-52 days after treatment. The trials were not in accord with GAP in the USA or other countries, so no maximum residue level could be estimated.

Twenty nine trials on peaches were conducted in the USA and one in Italy at rates equivalent to 2.7 and 1.7 times the maximum national registered rates respectively. The residues in the whole fruit were <0.01-0.16 mg/kg at the earliest sampling intervals, after treatment at stages from pre-flowering to immature fruit. As the trials did not comply with GAP in either Italy or the USA, the Meeting could not estimate a maximum residue level.

Berries and other small fruits. Supervised trials on grapes were conducted in Chile, Mexico, South Africa and the USA. In the US trials, residues were determined in raisins and raisin trash as well as grapes. GAP in Chile specifies rates of 6-8 kg ai/ha (in-furrow) or 2.8-4.8 kg ai/ha (drip irrigation), with a PHI of 45 days. Registered use patterns in Mexico are for 4-6 kg ai/ha and no specified PHI. In South Africa, a maximum rate of 1 g ai/m^2 is registered with a PHI of 100 days, and in the USA 3.3-6.5 kg ai/ha with a PHI of 2 days.

The Chilean and US trials were at GAP rates and above, up to 3 and 1.5 times the maximum rates in Chile and the USA respectively. Sampling was at longer intervals than the GAP PHI in many of the US trials, but the earliest sampling is considered to accord with GAP if mature fruit were collected. The residues in the grapes were <0.01-0.09 mg/kg from a total of 49 trials. The residues from trials which were considered to comply with GAP in rank order were <0.01 (11), 0.01 (6), 0.02 (7), 0.03 (5), <0.05 (4), 0.07 (2) and 0.09 mg/kg. Although analytical recoveries of fenamiphos were determined at concentrations of 0.01, 0.02, 0.03 and 0.05 mg/kg, recoveries of all components of the defined residue (fenamiphos, FSO and FSO_2) were determined only at concentrations of 0.05 and 0.1 mg/kg, so the validated limit of determination in grapes is 0.05 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg, confirming the existing CXL, and an STMR of 0.02 mg/kg (HR = 0.09 mg/kg).

Tropical fruits - inedible peel. Trials on bananas were conducted in Australia, Brazil, the Canary Islands (Spain), Costa Rica and the Windward Islands. Trials in the Canary Islands and the Windward Islands were evaluated against GAP for Spain and Costa Rica respectively. Rates at or above the registered use patterns were applied in the trials. In some cases rates of application were expressed both as kg ai/ha and as g ai/plant to allow for different cropping densities in different regions. For example the trials in Costa Rica allowed for cropping densities ranging from 416 to 833 plants/ha, and those in the Windward Islands for 412-1785 plants/ha. Although trials with the CS product were reported, the results were not used in the estimation of the maximum residue level or STMR because registration of the product was pending. The residues were determined separately in the pulp and peel or on a whole fruit basis; where residues in the pulp and peel were below the limit of detection or determination, the residues in the whole fruit were considered to have the same value.

The residues in the whole fruit in rank order were <0.01 (7) and <0.02 (3) mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg, based on the routine limit of quantification of fenamiphos, and recommended withdrawal of the existing CXL of 0.1 mg/kg. The residues in banana pulp in rank order were ≤0.02 (6) and <0.025 (3) mg/kg. An STMR of 0.02 mg/kg was estimated (HR = 0.025 mg/kg).

Trials on pineapples were mainly in Hawaii, with a few trials in Australia and Puerto Rico. Registered use patterns in Australia allow a maximum of 5 applications at 2.4 kg ai/ha to the main plant crop and ratoon crop and a maximum of 2 applications at 4.8 kg ai/ha to the ratoon crop alone; PHIs are not specified. Registered labels in the USA specify two use patterns, one for Puerto Rico and the other for Hawaii. For Puerto Rico, a pre-plant application of 10 kg ai/ha with additional applications at 5.4-9.8 kg ai/ha post-planting and to the first ratoon crop, with total applications of 20 kg ai/ha per ratoon crop are recommended, with a PHI of 225 days for the post-planting applications. In Hawaii the total applications are 26.2 kg ai/ha per plant crop and 9.8 kg ai/ha per ratoon crop, made up of a pre-planting application of 9.8 kg ai/ha for the plant crop and post-planting sprays at 0.5-3.3 kg ai/ha. A PHI of 30 days is recommended for the post-planting applications.

In the Hawaiian trials the rates were equivalent to 2.3 times the pre-planting application, 1.2-2.3 times the total plant crop treatment and up to 2.3 times the ratoon crop treatment. The residues were <0.01-0.03 mg/kg in the whole fruit and <0.01-0.05 mg/kg in the pulp. Residues were determined in bran, foliage, forage, crowns and stumps in addition to whole fruit and pulp.

In two Puerto Rican trials, twice the pre-plant rate and up to 1.1 times the post-plant rates were applied to the plant crop.

The residues in the whole fruit in the 3 Australian trials were <0.01 mg/kg, but only 1 trial complied with GAP. The residues in the pulp were <0.01 mg/kg in the Puerto Rican trials. Although the residues in the Hawaiian trials were from exaggerated treatments, the number of post-planting applications to the plant and ratoon crops are not always specified on the label, and multiple applications may be required at these stages depending upon pest pressure. Total application rates per plant crop and ratoon crop are indicated however. The Meeting considered that although treatments were exaggerated the residues in the whole fruit and pulp were below the limit of detection in most of the trials, so the results were acceptable for estimating a maximum residue level and an STMR. The residues in the whole fruit in rank order were <0.01 (8), 0.02 and 0.03 mg/kg, and in the pulp <0.01 (26), 0.01 (2), 0.02 (2), 0.05 and 0.14 mg/kg. The Meeting included the figure of 0.14 mg/kg in the data set, as the conditions of the trial (PHI, application rate and application timing) did not differ from other instances where residues in the pulp were <0.01 mg/kg. The validated limit of determination in pineapple pulp, bran, foliage and crowns was 0.05 mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg, confirming the existing CXL for pineapples, and an STMR of 0.01 mg/kg for pineapple pulp (HR = 0.14 mg/kg).

The residues in wet bran were <0.01-0.25 mg/kg, in dry bran <0.01-2.3 mg/kg and in unspecified bran <0.01-0.13 mg/kg.

Oilseeds. Supervised trials on peanuts were conducted in the USA and South Africa. The residues were determined in nuts, shells, foliage and vines. In the US trials, up to 7 times the maximum registered rate was applied and nuts were sampled at normal harvest. Residues in all samples of nuts were below the limit of detection or determination. The residues in vines were <0.01-3.19 mg/kg at rates of 4.7-7 times the label rate and PHIs of 94-154 days after planting. GAP in the USA allows single applications at rates of 1.6-2.9 kg ai/ha, with no specified PHI. In South Africa, the registered use pattern is a single application at 1.6-3.2 kg ai/ha and a PHI of 63 days. Although exaggerated treatments were applied, no residues were detectable in the nuts and the Meeting therefore concluded that the existing CXL of 0.05* mg/kg could be supported. The Meeting estimated an STMR of 0, as no residues were detectable in any samples. It was considered that owing to the high oil content of peanuts residues might accumulate in the nuts, but this was not found (HR = 0.01 mg/kg for peanut).

In trials on cotton seed in Brazil, South Africa and the USA fenamiphos was applied before or shortly after planting. In the US trials the rates were 0.6-1.7 times the maximum registered rate. GAP in the USA requires application at 0.82-3.27 kg ai/ha with no specified PHI, in Brazil 3-5 kg ai/ha with a PHI of 98 days, and in South Africa 15 g ai/100m of row with no specified PHI. Residues were determined in seed (delinted and fuzzy) and ginned trash. The residues in the cotton seed in all the relevant trials (25) were <0.01 mg/kg. The Meeting estimated a maximum residue level of 0.05* mg/kg, confirming the existing CXL, as this was the validated limit of determination. An STMR of 0.01 mg/kg was estimated (HR = 0.01 mg/kg).

The residues in the cotton gin trash were <0.01 mg/kg in 7 trials which were considered to conform to US GAP.

Coffee. Supervised trials were conducted in Brazil, Guatemala and Mexico. In all the trials a single soil application was made to mature trees at the pre-bloom or fruit formation stage. Residues were determined in the fruit (berries) and the beans. The MRL applies to the seed only; the bean and other parts of the fruits are not included.

GAP in Brazil is 1-7 g ai/plant with a PHI of 45 days, in Guatemala 2.4-5 kg ai/ha and a PHI of 60 days, and in Mexico 1-1.5 g ai/plant with a PHI of 45 days. The Mexican trials were not considered, as the prescribed GAP could not be compared with the application rate as expressed in the supervised trials. The residues in the two relevant samples of beans were <0.1 and <0.2 mg/kg. The residues in the berries in rank order were 0.01 (3), 0.02, 0.03, 0.04, <0.05 (4), 0.06 and 0.11 mg/kg. The Meeting did not estimate a maximum residue level as there were insufficient data for beans, and recommended withdrawal of the existing CXLs of 0.1 mg/kg for coffee beans and coffee beans, roasted.

Dietary burden of livestock and animal feeding studies

Tables of dietary burden were compiled for dairy cattle and hens, in which maximum and median residues in various feed items were listed together with an indication of the percentage dry matter, percentage of the item in the diet, and the intake expressed as mg/animal/day. Commodities in which the dry matter was above 85% as received were not corrected for dry matter.

For dairy cattle, a dry matter intake of 15 kg/day for a 500 kg animal was assumed. An exposure of 0.13 ppm in the feed (1.88 mg/animal/day; 0.004 mg/kg body weight/day) was estimated on the basis of the consumption of dry apple pomace, raisin trash, peanut vines and dry tomato pulp, which provided the highest median intake. As a typical diet would not consist only of these items the estimate is probably exaggerated. The lowest level in the diet in the cattle feeding study was 2 ppm fenamiphos sulfoxide or about 15 times the calculated exposure. After feeding at 2 ppm for 28 days residues in the milk, liver, kidney, muscle (flank and loin) and fat (omental, subcutaneous and renal) were below the limits of detection of 0.001 mg/kg in milk and 0.01 mg/kg in tissues. The limits of determination were reported as 0.005 mg/kg in milk and 0.01 mg/kg in tissues. On the basis of these limits the Meeting estimated maximum residue levels of 0.005* mg/kg in milk and 0.01* mg/kg in the tissues. STMRs of 0 were estimated for milk, meat and edible offal, since no residues were detectable in any tissues after feeding at 15 times the calculated exposure level for a dairy animal.

For hens, an intake of 150 g dry matter/day and 2 kg body weight were assumed. An estimated maximum exposure of 0.01 ppm in the feed was based on 100% peanut meal as a worst-case situation, as only peanut meal and cotton meal were included in the dietary burden table. The lowest feeding levels in two studies with labelled fenamiphos were 0.06 and 2 ppm for 14 consecutive days. The total radioactivity from the 0.06 ppm level in eggs or tissues was not reported. With feeding at 2 ppm the maximum radioactivities in the tissues were below the minimum quantifiable limits of 7 to 20 ng/g (ppb) as fenamiphos. On the assumption that the limit of determination reported in cattle tissues is also applicable to poultry tissues and eggs, the Meeting estimated maximum residue levels of 0.01* mg/kg for poultry meat, poultry offal and eggs. It should be noted that the calculated exposure of 0.002 ppm in the hen diet is probably exaggerated as feeding 100% peanut or cotton meal would not be considered typical. STMRs of 0 were estimated for eggs, poultry meat and poultry offal.

Processing

Processing studies on tomatoes, oranges, apples, grapes and pineapples were reported.

Tomatoes containing residues of 0.5 mg/kg fenamiphos were subjected to commercial processing into canned tomatoes, juice and ketchup. Total fenamiphos residues were concentrated in tomato pulp solids (wet and dry) and tomato pomace, as well as other commodities that may be used as animal feed items. Calculated processing factors for tomato juice, pasteurised tomato juice, ketchup and canned tomatoes were 0.74, 0.88, 0.58 and 0.72 respectively. As an STMR of 0.05 mg/kg was estimated for whole tomatoes, an STMR of 0.05 mg/kg was also estimated for tomato juice (HR-P = 0.27 for tomato juice).

Tomatoes fortified with [U-*phenyl*-^{14}C]fenamiphos at 0.8 mg/kg were allowed to stand at room temperature for 24 hours then blanched, peeled, cored, and cooked for 40 minutes. Blanching and cooking led to a reduction of residues by almost 50%, with 27% of the radioactivity present in the cooking water. There was negligible loss of radioactivity (1.5%) by peeling and coring.

Orange trees were treated at a rate equivalent to 100 kg ai/ha and fruit were harvested and processed when residues had reached maximum levels in the leaves, which were sampled at monthly intervals after treatment. The residues in the whole fruit ranged from <0.01 to 0.13 mg/kg, with average residues of 0.07 mg/kg. The residues were concentrated in unwashed and washed peel, peel bits, clear oil (produced from the peel), chopped peel, pressed dry peel, press liquor and molasses, with processing factors of 6.71, 8.57, 3.28, 64, 1.86, 5.71, 2.86 and 7.0 respectively. Processing

factors for juice and pulp were 0.28 and 0.14 respectively. STMRs were not calculated for the processed fractions as no maximum residue level was estimated for oranges or citrus fruits.

Apple trees were treated with a soil application at 33.6 kg ai/ha. Fruit were harvested 66 days after treatment and processed into juice and pomace. The residues in the apples were 0.14 mg/kg and were concentrated in wet and dry pomace with processing factors of 4.86 and 17.7 respectively. A processing factor of 0.78 was calculated for apple juice. As an STMR of 0.01 mg/kg was estimated for apple an STMR of 0.0078 mg/kg was calculated for juice.

Grapes were processed after treatment at rates of one and 5 times the maximum registered rate in the USA. The residues in fruit were 0.07, 0.02 and 0.02 mg/kg at 55, 56 and 7 days after treatment respectively at 1, 1 and 5 times rates. Fenamiphos residues were concentrated in raisins, raisin trash and dry pomace, with processing factors of 1.57, 8.3 and 5 respectively. Processing factors for juice and wet pomace were <1. An STMR of 0.009 mg/kg was calculated for juice (HR-P for raisins = 0.14 mg/kg; grape juice = 0.04 mg/kg).

Pineapples were processed into raw juice, canned juice, raw bran and dried bran. The residues in the whole fruit were 0.67 mg/kg after 7 applications at 5 times the registered US rate for Hawaii. The residues were concentrated in canned juice, raw bran and dried bran with calculated processing factors of 1.2, 2.1 and 2.5 respectively. STMRs of 0.006 and 0.012 mg/kg were calculated for raw and canned juice (HR-P = 0.17 mg/kg for pineapple juice, canned).

Peanuts were treated with 5 times the maximum registered US rate at the mid to late pegging stage. The residues in the kernels were 0.01 mg/kg. The peanuts were processed into meal, soapstock, crude oil and refined oil. The residues were ≤0.01 mg/kg in all the fractions except crude oil which contained 0.02 mg/kg. This was not considered to be a concentration effect as the refined oil contained <0.01 mg/kg. An STMR of 0 was estimated for peanuts, so the STMR for peanut oil is the same. The Meeting estimated a maximum residue level of 0.05* mg/kg for peanut oil, crude.

The residues in cotton seed were 0.01 mg/kg after a single exaggerated application at planting. Cotton bolls were harvested at maturity 153 days after treatment. The seed was processed into meal, hulls, soapstock, crude oil and refined oil. The residues in all the processed fractions were ≤0.01 mg/kg, except in crude oil which contained 0.02 mg/kg. This was not considered to be a concentration effect. The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.01 mg/kg for cotton seed oil, crude.

The Meeting recommended withdrawal of the following existing CXLs which were not supported by data: broccoli, cauliflower, kiwifruit, soya beans, sugar beet and sweet potato.

RECOMMENDATIONS

On the basis of the data from supervised trials, the Meeting estimated the maximum residue and STMR levels shown below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with the MRL and for estimation of dietary intake: “sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos”.

Commodity		MRL, mg/kg		STMR,	HR/HR-P
CCN	Name	New	Previous	mg/kg	mg/kg
FP 0226	Apple	0.05*		0.01	0.01
JF 0226	Apple juice			0.0078	0.0078
FI 0327	Banana[1]	0.05*	0.1	0.02	0.025
VB 0400	Broccoli	W	0.05*		
VB 0402	Brussels sprouts	0.05	0.05*	0.01	0.01
VB 0041	Cabbages, Head[1,2]	0.05	0.05*	0.01	0.05
VR 0577	Carrot[1,2]	0.2	0.2	0.02	0.08

Commodity		MRL, mg/kg		STMR,	HR/HR-P
CCN	Name	New	Previous	mg/kg	mg/kg
VB 0404	Cauliflower	W	0.05*		
SB 0716	Coffee beans	W	0.1		
SM 0716	Coffee beans, roasted	W	0.1		
SO 0691	Cotton seed	0.05*	0.05*	0.01	0.01
OC 0691	Cotton seed oil, crude	0.05*		0.01	
MO 0105	Edible offal (Mammalian)	0.01*		0	
PE 0112	Eggs	0.01*		0	
FB 0269	Grapes [1,2]	0.1	0.1	0.02	0.09
JF 0269	Grape juice			0.009	0.04
FI 0341	Kiwifruit	W	0.05*		
MM 0095	Meat (Mammalian)	0.01*		0	
VC 0046	Melons, except Watermelon[1,2]	0.05*	0.05*	0.02	0.02
ML 0106	Milks	0.005*		0	
FC 0004	Oranges, Sweet, Sour	W	0.5		
SO 0697	Peanut	0.05*	0.05*	0	0.01
OC 0697	Peanut oil, crude	0.05*		0	
VO 0051	Peppers [1,2]	0.5		0.055	0.35
FI 0353	Pineapple [1,2]	0.05*	0.05*	0.01	0.14
JF 0341	Pineapple juice, canned			0.012	0.17
	Pineapple juice, raw			0.006	
VR 0589	Potato	W	0.2		
PO 0111	Poultry, Edible offal of	0.01*		0	
PM 0110	Poultry meat	0.01*		0	
VD 0541	Soya bean (dry)	W	0.05*		
VR 0596	Sugar beet	W	0.05*		
VR 0508	Sweet potato	W	0.1		
VO 0448	Tomato [1,2]	0.5	0.2	0.05	0.30
JF 0448	Tomato juice			0.05	0.27
VC 0432	Watermelon [1,2]	0.05*		0.02	0.02

HR: highest residue in edible portion of raw commodity from supervised trials
HR-P: highest residue in processed commodity, calculated from the HR and the processing factor
[1] The information provided to the JMPR precludes an estimate that the acute dietary intake for children would be below the acute reference dose.
[2] The information provided to the JMPR precludes an estimate that the acute dietary intake for the general population would be below the acute reference dose.

DIETARY RISK ASSESSMENT

Chronic intake

STMRs were estimated for all commodities included in the dietary intake assessment. International Estimated Daily Intakes for the five GEMS/Food regional diets were in the range of 3-14% of the ADI (Annex III).

The Meeting concluded that the intake of residues of fenamiphos resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The acute reference dose for fenamiphos is 0.0008 mg/kg bw as the available data did not permit the 1997 Meeting to establish an acute reference dose different from the ADI. The calculated short-term intakes ranged from 15 to 2900% of the acute reference dose for children and 8 to 863% of the acute reference dose for the general population (Annex IV). It should be noted that for commodities such as apples, bananas, melons, peanuts and watermelons, residues in the edible portion in all supervised trials were below the limit of detection of the method used, but for the purposes of the short-term risk assessment figures at the limit of detection were used in the calculation. The current method does not allow any further refinement of the acute intake assessment.

The Meeting concluded that all commodities should be considered further when an acute reference dose is established from new data or when new data on unit weight, variability factor etc. become available.

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FENPROPIMORPH (188)

EXPLANATION

Fenpropimorph was first evaluated for residues by the 1995 JMPR. That Meeting estimated maximum residue levels which were recommended for use as MRLs for cereals (barley, oats, rye and wheat), cereal straw and fodder (dry), sugar beet, and fodder beet leaves or tops. Further work or information was desirable, among other items, on livestock and poultry feeding studies with determination of fenpropimorph and the major metabolites identified in the metabolism studies (e.g. BF 421-1, BF 421-2 and BF 421-3), and validated analytical regulatory methods (including representative chromatograms) for the determination of fenpropimorph and its major metabolites in animal products.

The 1997 CCPR noted that animal transfer studies were being developed (ALINORM 97/24A, para 77). The 1998 CCPR noted such studies would be available to the 1999 JMPR and that the draft MRL for sugar beet should be 0.05 mg/kg (*). The Committee postponed discussions and scheduled the residue evaluation of fenpropimorph for the 1999 JMPR (ALINORM 99/24, para 80 and Appendix II).

Information on GAP, a dairy cattle feeding study, an analytical method for animal products, and a metabolism study and residue trials on bananas were reported to the present Meeting by the manufacturers (Burkey, 1997). Information on national MRLs and GAP was provided by Poland and The Netherlands, and on GAP by Germany and the UK.

METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

Hamm (1997) treated banana plants four times at the twofold application rate of 0.9 kg ai/ha with [*morpholine*-2,6-^{14}C] and [U-*phenyl*-^{14}C]fenpropimorph. Because in commercial practice growing bunches are protected against insects by a plastic bag which can be destroyed leaving the fruit unprotected, trials were on bagged and unbagged bananas. The intervals between the four applications were 14, 51 and 12 days. All samples were taken one day after the last application.

Table 1. Total radioactive residues in bananas, mg/kg as fenpropimorph (Hamm, 1997).

Sample	Unripe unbagged		Ripe unbagged		Unripe bagged		Ripe bagged	
	morpholine label	phenyl label	morpholine label	phenyl label	Morpholine Label	phenyl label	morpholine label	phenyl label
Peel	0.42	0.22	0.41	0.19	0.18	0.038	0.22	0.04
Pulp	0.79	0.042	0.73	0.025	0.43	0.018	0.38	0.017
Whole fruit	0.67	0.105	0.61	0.094	0.35	0.025	0.32	0.026

On a whole fruit basis, the maximum TRR from the morpholine label was about 0.67 mg/kg in unripe, unbagged and 0.61 mg/kg in ripe, unbagged bananas. The corresponding residues in bagged bananas were 0.35 and 0.32 mg/kg. Phenyl-labelled bananas contained significantly lower TRRs: 0.11 mg/kg (unripe, unbagged) and 0.09 mg/kg (ripe, unbagged), with corresponding residues in bagged bananas of 0.025 and 0.026 mg/kg (Table 1).

About 73–88% of the TRR in whole ripe fruit and 27% to 72% of that in unripe fruit was extractable with methanol (Table 2).

Table 2. Methanol-extractability of ^{14}C in whole bananas (Hamm, 1997).

	^{14}C fenpropimorph , mg/kg and (% of TRR)							
	Unbagged ripe fruit		Unbagged unripe fruit		Bagged unripe fruit		Bagged unripe fruit	
	morpholine label	phenyl label	morpholine label	phenyl label	morpholine label	phenyl label	morpholine label	phenyl label
TRR	0.61 (100)	0.094(100)	0.67 (100)	0.11 (100)	0.32 (100)	0.026(100)	0.35 (100)	0.025 (100)
MeOH extract	0.51 (83)	0.078 (88)	0.14 (27)	0.082 (72)	0.23 (73)	0.021 (84)	0.07 (27)	0.014 (49)
Residue	0.097 (17)	0.014 (14)	0.5 (68)	0.023 (29)	0.01 (31)	0.005 (17)	0.26 (69)	0.011 (55)

The TRR is higher in fruit treated with morpholine-labelled than phenyl-labelled fenpropimorph because the morpholine ring can be opened and the resulting ^{14}C fragments incorporated during assimilation processes in leaves and growing and ripening fruits. The assimilation products are translocated from leaves, and to some extent from fruits, by the phloem to the storage parenchyma of the bananas and transformed to starch which is enzymatically hydrolysed to mono- and disaccharides during ripening. The highest content of ^{14}C-labelled sugars (76% of the TRR) was found in unbagged ripe fruit. No ^{14}C can be incorporated from the phenyl label, so the TRR is low.

The methanol extract of morpholine labelled samples showed two major HPLC peaks, one non-polar identified by MS as fenpropimorph, and the other polar identified by acetylation and HPLC as a mixture of the natural assimilation products glucose, fructose and saccharose. Phenyl-labelled samples showed only one prominent HPLC peak which was identified as fenpropimorph. Table 3 shows the residues of the unchanged parent.

Table 3. [^{14}C]fenpropimorph found in banana metabolism study (Hamm, 1997).

Banana sample	Fenpropimorph, mg/kg, and % of TRR			
	Morpholine label		Phenyl label	
	mg/kg	% TRR	mg/kg	% TRR
Unbagged, unripe	0.07	15.5	0.064	60.5
Unbagged, ripe	0.017	3.2	0.038	34.9
Bagged, unripe	0.022	10.7	0.008	34.7
Bagged, ripe	0.012	4.4	0.005	13.7

METHODS OF RESIDUE ANALYSIS

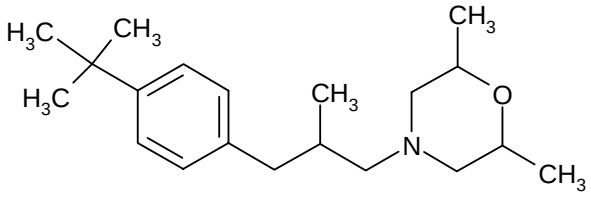
Analytical methods

Analytical methods for fenpropimorph in bananas and the metabolite BF 421-2 in animal products were reported. The structures and chemical names of the two compounds are shown in Figure 1.

Bananas. BASF method 241/1 (JMPR 1995) was modified to determine residues of fenpropimorph in bananas (Tilting, 1993; Zehr, 1997). Fenpropimorph is distilled from the fruit after mixing with aqueous sodium bicarbonate solution in Bleidner apparatus and the distillate is collected in dichloromethane. After clean-up by liquid/liquid partition and a cation-exchange column, the residues are quantified by GLC with an NPD. The LOD for whole fruit and pulp is 0.05 mg/kg (Table 4).

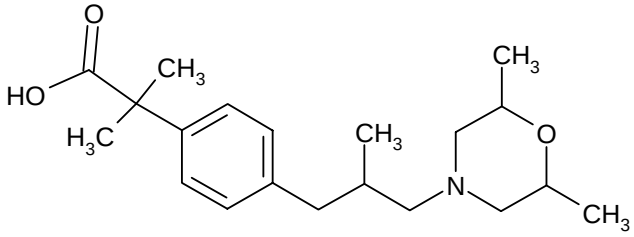
Figure 1: Structures and chemical names

fenpropimorph



Chemical name: (±)cis-4-[3-(4-*tert*-butyl phenyl)-2-methyl propyl]-2,6-dimethyl morpholine

BF 421-2



Chemical name: 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid

Table 4. Validation of analytical method 241/1 for bananas (Tilting, 1993).

Sample	Fortification levels, mg/kg	Average recovery of fenpropimorph, % ± SD (n = 4)
Banana pulp	0.05	96 ± 6
	5	91 ± 15
Banana peel	0.05	92 ± 2
	5	87 ± 15
Whole banana	0.05	97 ± 6
	5	96 ± 3

The method was validated by an independent laboratory (Arzt and Malinsky, 1997). Shaffer (1997a) used GC-MS to test specificity. Fenpropimorph has been tested through the Pesticide Analytical Manual Volume I multiresidue methods by Fomenko (1996).

Multiresidue method. The official method of analysis in The Netherlands (Olthof, 1999) describes the determination of fenpropimorph residues in fatty and non-fatty foods by GLC with an ion trap detector. The LOD is 0.05 mg/kg.

Animal products. The method (Tribolet, 1995) determines fenpropimorph acid (BF 421-2), which is the major metabolite of fenpropimorph in animal tissues, eggs and milk. The limits of determination are 0.01 mg/kg for animal tissues and eggs, and 0.002 mg/l for milk.

Milk and eggs are extracted with acetonitrile and pH 9 buffer. After filtration the acetonitrile is evaporated and the residue is redissolved in methanol, diluted with water and pH 9 buffer, and purified by partitioning with hexane. The analyte, which remains in the aqueous phase, is cleaned up on a C-18 bonded silica gel column. Determination is by HPLC with UV detection. Tissues are extracted directly with methanol and pH 9 buffer and the analysis is completed as above.

Validation showed mean recoveries from the individual substrates and an overall mean recovery within the range of 70-110%. All standard deviations were <20%. The repeatability and reproducibility were tested with meat and milk. For the repeatability the difference between the minimum and maximum individual recovery value in one laboratory was 19% and 13% for meat and milk, respectively. For the reproducibility the difference between the minimum and maximum individual recovery value of two laboratories was 33% and 45% for meat and milk, respectively (see Tables 5 and 6).

Table 5: Recoveries of BF 421-2 from animal products (Tribolet, 1995).

Sample	Fortification, mg/kg	Control, mg/kg	Recovery, %	Mean, %	SD_{abs}	SD, %	n
Meat Laboratory 1	0.01 0.1	<0.01	100, 103, 108, 105, 105, 97, 105, 116 94, 98, 96, 95, 98, 101, 95, 97	105 97	5.6 2.3	5.4 2.3	8 8
Meat Laboratory 2	0.01	<0.01	83, 100, 84				3
Milk Laboratory 1	0.002 mg/l 0.02 mg/l	<0.002	94, 94, 94, 99, 105, 107, 105, 105 85, 91, 89, 86, 75, 84, 87, 89	100 86	5.8 4.9	5.7 5.7	8 8
Milk Laboratory 2	0.002 mg/l	<0.002	63, 65, 62				3
Liver Laboratory 1	0.01 0.1	<0.01	81, 98, 92 103, 101, 106	97	9.1	9.4	6
Kidney Laboratory 1	0.01 0.1	<0.01	94, 89, 89 98, 96, 96	94	3.8	4.1	6
Eggs Laboratory 1	0.01 0.1	<0.01	70, 66, 80 78, 77, 74	74	5.3	7.2	6

Table 6: Overall recoveries of BF 421-2 in animal products (Tribolet, 1995).

Sample	n	Recovery, % (from Table 5)			Mean recovery, %	SD, %
		minimum	maximum	difference		
Meat	19	83	116	33	99	7.7
Milk	19	62	107	45	88	16
Liver	6	81	106	25	97	9.4
Kidney	6	89	98	9	94	4.1
Egg	6	66	80	14	74	7.2

Stability of residues in stored analytical samples

Bananas. In the supervised trials on bananas the longest period that samples were stored frozen before analysis was 7.5 months. The storage stability of fenpropimorph in whole bananas was determined during this period (Shaffer, 1997b). Control samples of whole bananas were fortified with fenpropimorph at 1 mg/kg and re-analysed after 1, 2, 3 and 7.5 months (Table 7).

Table 7. Storage stability of fenpropimorph in bananas (Shaffer, 1997).

Storage period, months	% remaining	Procedural recovery, %	Mean corrected % remaining
1	67, 75	87	82
2	76, 76	78	97
3	86, 78	85	96
7.5	68, 69	72	95

Animal products. Samples fortified with known amounts of BF 421-2 were stored at -18°C for similar periods to those in the cattle feeding trials. The results are shown in Table 8.

The average percentage of the added BF 421-2 remaining after storage was found to be 66% for muscle, 81% for milk, 92% for liver, 95% for kidney, 74% for fat and 76% for blood. The freshly fortified samples were not analysed.

Table 8: Storage stability of BF 421-2 in animal products (Tribolet, 1999).

Sample	Sample size	Fortification level	Storage period	BF 421-2, mg/kg or mg/l	Average, %[1]
Muscle	5 g	0.1 mg/kg	26 Mar-01 Dec.	0.058 / 0.064, 0.054 / 0.059 0.082 / 0.077[2]	66
Liver	5 g	0.1 mg/kg	26 Mar-01 Dec.	0.092, 0.092, 0.092	92
Kidney	5 g	0.1 mg/kg	26 Mar-01 Dec.	0.094, 0.095, 0.097	95
Fat	5 g	0.1 mg/kg	26 Mar-04 Jan. 1999	0.076, 0.073, 0.073	74
Milk	10 ml	0.02 mg/l	19 Mar-27 Oct.	0.018, 0.016, 0.015, 0.016, 0.016	81
Blood	1 ml	0.04 mg/l	26 Mar-30 Nov.	0.030, 0.034, 0.030, 0.030, 0.028	76

[1] Average remaining expressed as percentage of nominal value. The results are not corrected for individual procedural recoveries which were muscle 113, 97, 103, 108%; kidney 105, 108%; liver 103, 107%; fat 95, 88%; blood 78, 82%; milk 81, 70%.

[2] The three samples were analysed twice.

Definition of the residue

The 1995 JMPR concluded that for regulatory purposes the residue in plants should be defined as fenpropimorph. For risk assessment purposes, the data suggested that the total residues of fenpropimorph plus its major plant metabolites will almost certainly be no more than 3 times the level of fenpropimorph alone, but probably less than twice that level. No definition was proposed for animal products.

The current Meeting agreed that the definition of the residue for compliance with MRLs for plant commodities should be fenpropimorph *per se*. On the evidence of the metabolism in bananas, the same definition would be acceptable for the estimation of dietary intake in bananas.

In goats, no parent compound was found and the metabolite 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid (BF 421-2) was the major component of the residue. The metabolite 421-1 is present only in the fat, and BF 421-3 at lower concentrations in the kidneys, milk whey and fat. Conjugates of BF 421-2 were found in goat liver (1995 JMPR evaluations, Table 3, p.192).

In hens, although 3-10 unidentified metabolites were detected and measured as fenpropimorph equivalents in the organosoluble or water-soluble fractions of excreta, eggs, muscle, fat, skin and gizzard, compounds were identified and determined only in the plasma, liver and kidneys. The parent compound was detected only in the kidneys. No conjugates were found in hens (1995 JMPR, evaluations, Table 6 p.195).

On the basis of the metabolism studies on lactating goats reviewed by the 1995 JMPR, the current Meeting agreed that the definition of the residue for compliance with MRLs for animal products should be BF 421-2, expressed as fenpropimorph, and that the same definition was suitable for the estimation of dietary intake.

The Meeting agreed to recommend the following residue definitions.

Commodities of plant origin for both compliance with MRLs and the estimation of dietary intake: *fenpropimorph.*

Commodities of animal origin for compliance with MRLs and the estimation of dietary intake: *2-methyl-2-{4-[2-methyl-3-(cis-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid, expressed as fenpropimorph.*

USE PATTERN

Fenpropimorph is used in combination with other fungicides mainly in cereals. Tables 9 and 10 show the new information on GAP submitted by the manufacturers and governments to the present Meeting. Other uses are listed in the 1995 JMPR residue evaluation. Variations in PHIs are based on the GAP for the other fungicides in the registered formulations.

Formulations listed in Table 9

250EC 250 g/l fenpropimorph + 133 g/l bromuconazole
250EC 250 g/l fenpropimorph + 167 g/l bromuconazole
250EC 250 g/l fenpropimorph + 84 g/l epoxiconazole
270EC 270 g/l fenpropimorph + 480 g/l fenpropidin
275EC 275 g/l fenpropimorph + 160 g/l flusilazole + 100 g/l tridemorph
300EC 300 g/l fenpropimorph + 200 g/l tebuconazole
300EC 300 g/l fenpropimorph + 125 g/l propiconazole
300EC 300 g/l fenpropimorph + 300 g/l prochloraz
375EC 375 g/l fenpropimorph + 125 g/l propiconazole
375EC 375 g/l fenpropimorph + 160 g/l flusilazole
750EC 750 g/l fenpropimorph
250EW 250 g/l fenpropimorph + 67 g/l quinoxyfen
150SE 150 g/l fenpropimorph + 125 g/l epoxiconazole + 125 g/l kresoxim-methyl
187SE 187 g/l fenpropimorph + 250 g/l chlorothalonil
233SE 233 g/l fenpropimorph + 65 g/l quinoxyfen
250SE 250 g/l fenpropimorph + 84 g/l epoxiconazole
280SE 280 g/l fenpropimorph + 100 g/l azoxystrobin
300SE 300 g/l fenpropimorph + 150 g/l kresoxim-methyl

Table 9. Registered uses of fenpropimorph on cereals, grasses and oilseeds (foliar spray unless indicated as seed treatment).

Crop	Country	Form.	Application				PHI, days
			Time, growth stage	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Barley	Germany	300 EC	Spring, beginning of infection	0.3	0.075	2	35
		300 SE		0.21	0.053-0.11	2	35
		250 SE		0.38	0.094-0.19	2	35
		150 SE		0.15	0.038	2	35
		233 SE	Spring, up to stage 49 beginning of infection	0.35	0.087-0.18	2	49
	Poland	250 SC	From end of tillering to beginning of earing	0.25	0.06-0.12	1-2	35
		750 EC		0.75	0.19-0.37	1-2	35
Barley, spring	Netherlands	750 EC 250 EC	At infestation, between tillering and emergence of ears	0.75 0.38	0.13-0.38 0.063-0.19	1-2	42
		300 SE	At infestation, Feekes 4-5	0.21	0.035-0.11	1-2	35
	Poland	300 SE	From end of tillering to beginning of earing	0.15-0.21	0.04-0.1	1-2	35
		300 EC		0.3	0.08-0.15	1-2	35
	UK	250 EW	Before first spikelet of inflorescence visible	0.38		2	60
		270 EC	Before start of anthesis	0.27		2	50
		275 EC	Before early milk stage	0.28		2	40
		300 EC		0.3		2	35
		150 SE	Up to and including ear emergence just complete	0.15		2	50
		250 SE		0.38		2	50
		280 SE		0.56		2	35
		300 SE		0.21		2	50
Barley, winter	Netherlands	250 EC	At infestation, between tillering and emergence of ears	0.38	0.063-0.19	1-2	42
		300 SE	At infestation, Feekes 4-5	0.21	0.035-0.11	1-2	35
	Poland	300 SE	From end of tillering to beginning of earing	0.15-0.21	0.04-0.1	1-2	35
		300 EC		0.3	0.08-0.15	1-2	35
	UK	750 EC	Maximum of 2 treatments in year of harvest Maximum of 3 treatments in year of harvest	0.75 or 0.56		3 or 4	35
		250 EC	Before third node and/or before grain watery ripe stage	0.48 0.38		1 1	70 40
		270 EC	Before start of anthesis	0.27		2	50
		275 EC	Before early milk stage	0.28		2	40
		300 EC[1]		0.45		2	42
		300 EC[2]	Up to and including ear emergence complete	0.38		2	50
		150 SE		0.15		2	50
		250 SE		0.38		2	50
		300 SE		0.21		2	50
		300 EC[3]		0.3		3	35
		375 EC[4]	Before early milk stage	0.38		2	40
		375 EC[1,3]		0.38		3	35
		250 EW	Before first spikelet of inflorescence visible	0.38		2	60
		280 SE		0.56		2	35
Dandelion	Germany	750 EC	Spring, beginning of infection	0.75	0.13	2	35
Grasses	Netherlands	750 EC		0.75	0.38	1-2	28[5]
Linseed	UK	43 SC	Seed treatment		0.095	1	150
Oats	Netherlands	750 EC	As soon as mildew is visible on third upper leaf	0.75	0.13-0.38	1	42
Oats, spring	UK	300 EC		0.3		2	35
		250 EW	Before first spikelet of inflorescence visible	0.38		2	60

Crop	Country	Form.	Application				PHI, days
			Time, growth stage	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Oats, winter	UK	750 EC	Maximum of 2 treatments in year of harvest Maximum of 3 treatments in year of harvest	0.75 or 0.56		3 or 4	35
		300 EC		0.3		3	35
		250 EW	Before first spikelet of inflorescence visible	0.38		2	70
Rape	UK	43 SC	Seed treatment		0.095	1	135
Rye	Germany	300 EC	Spring, beginning of infection	0.3	0.075	2	35
		300 SE		0.21	0.053-0.11	2	35
		150 SE		0.15	0.038	2	35
		250 SE		0.38	0.094-0.19	2	35
	Netherlands	750 EC	At infestation, from emergence of last leaf until beginning of blossoming	0.75	0.13-0.38	1	42
	Poland	300 SE	From beginning of shooting to beginning of earing	0.15-0.21	0.04-0.1	1-2	35
		250 SC		0.25	0.06-0.12	1-2	35
		300 EC		0.3	0.08-0.15	1-2	35
		750 EC		0.75	0.19-0.37	1-2	35
	UK	250 EW	Before first spikelet of inflorescence visible	0.38		2	60
Rye, winter	Netherlands	250 EC	At infestation	0.38	0.063-0.19	1-2	42
	UK	750 EC	Maximum of 2 applic. in year of harvest Maximum of 3 applic. in year of harvest	0.75 or 0.56		3 or 4	35
Triticale	Germany	250 SE	Spring, beginning of infection	0.38	0.094-0.19	2	35
		150 SE		0.15	0.038	2	35
	UK	250 EW	Before first spikelet of inflorescence visible	0.38		2	70
Triticale, winter	UK	750 EC	Maximum of 2 applic. in year of harvest Maximum of 3 applic. in year of harvest	0.75 or 0.56		3 or 4	35
Wheat	Germany	750 EC	Spring, beginning of infection	0.75	0.13	2	35
		300 EC		0.3	0.075	2	35
		150 SE		0.15	0.038	3	35
		250 SE		0.38	0.094-0.19	2	35
		300 SE		0.21	0.053-0.11	2	35
		233 SE	Spring, up to stage 49 beginning of infection	0.35	0.087-0.18	2	49
	Poland	750 EC	From beginning of shooting to end of earing	0.75	0.19-0.37	1-2	35
		250 SC		0.25	0.06-0.12	1-2	35
Wheat, durum	UK	250 EW	Before first spikelet of inflorescence visible	0.38		2	70
Wheat, spring	Netherlands	250 EC	At infestation, from emergence of last leaf until blossoming	0.38	0.063-0.19	1	42
		375 SC	At infestation, from ear emergence until beginning of blossoming	0.38	0.063-0.19	1	42
		300 SE	At infestation, Feekes scale 4-5	0.21	0.035-0.11	1-2	35
	Poland	300 SE	From beginning of shooting to end of earing	0.15-0.21	0.04-0.1	1-2	35
		300 EC		0.30	0.08-0.15	1-2	35
	UK	750 EC		0.75		2	35
		250 EC	Before third node detectable and/or before grain watery ripe stage	0.48 0.38		1 1	80 40
		300 EC[2]	Before grain milky ripe stage	0.38		2	40
		300 EC[3]		0.3		2	35

Crop	Country	Form.	Application				PHI, days
			Time, growth stage	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
		250 EW	Before first spikelet of inflorescence visible	0.38		2	70
		280 SE		0.56		2	35
Wheat, winter	Netherlands	250 EC	At infestation, from emergence of last leaf until blossoming	0.38	0.063-0.19	1	42
		375 SC	At infestation, from ear emergence until beginning of blossoming	0.38	0.063-0.19	1	42
		300 SE	At infestation, Feekes scale 4-5	0.21	0.035-0.11	1-2	35
	Poland	300 SE	From beginning of shooting to end of earing	0.15-0.21	0.04-0.1	1-2	35
		300 EC		0.3	0.08-0.15	1-2	35
	UK	250 EC	Before third node detectable and/or before grain watery ripe stage	0.48 0.38		1 1	90 40
		270 EC	Before start of anthesis	0.27		2	60
		275 EC	Before early milk stage	0.28		3	40
		300 EC[1]		0.45		2	42
		300 EC[2]	Before grain milky ripe stage	0.38		2	40
		300 EC[2]		0.3		3	35
		375 EC[4]	Before early milk stage	0.38		2	40
		375 EC[1,3]		0.38		3	35
		250 EW	Before first spikelet of inflorescence visible	0.38		2	70
		150 SE	Up to and including ear emergence just complete	0.15		2	50
		187 SE	Max. total dose per crop 1.1 kg ai/ha. Latest application before flowering	0.75			60
		250 SE	Up to and including flowering just complete	0.38		2	50
		300 SE		0.21		2	50
		280 SE		0.56		2	35

[1] Fenpropimorph + prochloraz
[2] Fenpropimorph + tebuconazole
[3] Fenpropimorph + propiconazole
[4] Fenpropimorph + flusilazole
[5] 28: for mown grass as feed or for grazing by cattle

Table 10. Registered uses of fenpropimorph on fruits and vegetables (outdoor).

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc,, kg ai/hl	No.	
Banana	Cameroon[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	Central America[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	Cuba	88 OL	Foliar spray	0.44	2.2	4-12	0
	Ivory Coast[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	Lesser Antilles[1]	88 OL	Foliar spray	0.44	2.2	2-5	0
	Philippines[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	South America[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
Beetroot	UK	750 EC	Foliar spray	0.75		2	21
Bilberry	UK	750 EC	Foliar spray	0.75		3	10
Brussels sprouts	UK	750 EC	Foliar spray	0.75		3-5	14
Cranberry	UK	750 EC	Foliar spray	0.75		3	10
Currant, Black, Red, White	UK	750 EC	Foliar spray	0.75		3	10

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc,, kg ai/hl	No.	
Dewberries (incl.boysen- and loganberry)	UK	750 EC	Foliar spray	0.75		3	10
Gooseberry	UK	750 EC	Foliar spray	0.75		3	10
Hops	UK	750 EC	Foliar spray		0.0375	6	10
Horseradish	UK	750 EC	Foliar spray	0.75		3	28
Leek	Netherlands	750 EC	Foliar spray	0.75	0.14-0.19	2-3	21
Parsley, root	UK	750 EC	Foliar spray	0.75		3	28
Parsnip	UK	750 EC	Foliar spray	0.75		3	28
Plantain	Cameroon[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	Central America[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	Cuba	88 OL	Foliar spray	0.44	2.2	4-12	0
	Ivory Coast[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	Lesser Antilles[1]	88 OL	Foliar spray	0.44	2.2	2-5	0
	Philippines[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
	South America[1]	88 OL	Foliar spray	0.44	2.2	4-12	0
Raspberries, Red, Black	UK	750 EC	Foliar spray	0.75		3	10
Salsify	UK	750 EC	Foliar spray	0.75		3	28
Strawberry	UK	750 EC	Foliar spray	0.75		3	10

[1] GAP pending

RESIDUES RESULTING FROM SUPERVISED TRIALS

In plants

Bananas (Table 11). Fenpropimorph is a fungicide of the morpholine group with a high level of activity against Black Sigatoka *(Mycospaerella fijiensis)* and Yellow Sigatoka *(Mycospaerella musicola)* in bananas. The compound is systemic. Registration is already approved in Cuba and is pending, with similar conditions, in several other countries. The formulated product to be used on banana crops is an oil liquid containing 880 g/l fenpropimorph.

Bananas were treated with about 0.5 kg ai/ha in 20 l/ha oil-water emulsion. The intervals between the applications were 15-20 days for the control of Black Sigatoka and 16-42 days for Yellow Sigatoka depending on the weather conditions and disease pressure. In view of the recommendation that no more than two consecutive treatments should be applied to control each of the insects involved (fungicide resistance management strategy for morpholine products) four applications have been considered to be the maximum number during the growth of individual banana bunches.

In eight supervised trials in 1994 in Martinique, a 750 g/l EC formulation was applied to bagged bananas from the ground with motorised knapsack mistblower sprayers (Tilting and Mackenrogh, 1995). The spray nozzle was directed vertically upwards between the banana plants so that the spray rose above them and was able to fall onto the upper leaves of the plant. In this way the spray application simulated aerial application.

Further trials in1996 in Costa Rica (4), Ecuador (4), Columbia (3), Honduras (2), Guatemala (1) and Mexico (1), were with the 880 g/l OL (Wofford and Artz, 1997). Each trial was with a control plot and a treated plot. Before the first application, bananas on half the trees in each plot were bagged. The fungicide was applied with motorised backpack mist blower sprayers at twelve sites. Applications at three sites were made by air with either a helicopter or fixed-wing aircraft at a target rate for each of the four applications of 0.545 kg ai/ha. The applications were 68, 56, 12 and 0 days before harvest.

Where residues were not detected, they are recorded in Table 11 as below the limit of determination (LOD). Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although all trials included control plots, no control results are recorded in the Table as none of the residues in control samples exceeded the LOD. The residues were not corrected for recovery.

Table 11. Residues of fenpropimorph in or on bananas.

Report No., Location, Country, Year	Form.	Type of application	Application rate			No. of treat-ments	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
RNC 95153 Pueblo Nuevo, Costa Rica, 1996	88 OL	Ground	0.44	20	2.2	4	Whole fruit (unbagged)	0	1.2
			0.62	20	3.1			5	0.72
			0.49	20	2.5		Pulp (unbagged)	0	0.30
			0.55	20	2.8			5	0.17
							Whole fruit (bagged)	0	0.13
								5	0.16
							Pulp (bagged)	0	0.08
								5	<0.05
RNC 95154 Santa Maria, Costa Rica, 1996	88 OL	Ground	0.61	20	3.1	4	Whole fruit (unbagged)	0	0.75
			0.56	20	2.8			5	0.38
			0.51	20	2.6			10	0.50
			0.55	20	2.8			15	0.32
								25	<0.05
							Pulp (unbagged)	0	0.22
								5	0.18
								10	0.29
								15	0.13
								25	<0.05
							Whole fruit (bagged)	0	0.37
								5	0.38
								10	0.40
								15	0.31
								25	<0.05
							Pulp (bagged)	0	0.20
								5	0.19
								10	0.19
								15	0.11
								25	<0.05
RNC 95155 Santa Maria, Costa Rica, 1996	88 OL	Ground	0.58	20	2.9	4	Whole fruit (unbagged)	0	1.4
			0.52	20	2.6			5	0.66
			0.59	20	3		Pulp (unbagged)	0	0.29
			0.56	20	2.8			5	0.43
							Whole fruit (bagged)	0	0.13
								5	0.33
							Pulp (bagged)	0	<0.05
								5	0.07
RNC 95156 Boliche, Ecuador, 1996 1996	88 OL	Ground	0.53	20	2.7	4	Whole fruit (unbagged)	0	0.26
			0.57	20	2.9			5	0.20
			0.62	20	3.1		Pulp (unbagged)	0	0.06
			0.56	20	2.8			5	0.06
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	<0.05

Report No., Location, Country, Year	Form.	Type of application	Application rate			No. of treat-ments	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
								5	<0.05
RNC 95157 Milagros, Ecuador, 1996	88 OL	Ground	0.59	20	2.9	4	Whole fruit (unbagged)	0	0.21
			0.56	20	2.8			5	0.36
			0.64	20	3.2		Pulp (unbagged)	0	<0.05
			0.56	20	2.8			5	<0.05
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	<0.05
								5	<0.05
RNC 95158 Marcelino, Ecuador, 1996	88 OL	Ground	0.51	20	2.6	4	Whole fruit (unbagged)	0	0.1
			0.52	20	2.6			5	0.06
			0.60	20	3.0		Pulp (unbagged)	0	<0.05
			0.52	20	2.6			5	<0.05
							Whole fruit (bagged)	0	0.17
								5	0.17
							Pulp (bagged)	0	0.07
								5	0.06
RNC 95159 Cienaga, Colombia, 1996	88 OL	Ground	0.52	20	2.6	4	Whole fruit (unbagged)	0	0.16
			0.52	20	2.6			5	0.08
			0.54	20	2.7			10	0.09
			0.51	20	2.5			15	0.11
								25	0.07
							Pulp (unbagged)	0	<0.05
								5	<0.05
								10	<0.05
								15	<0.05
								25	<0.05
							Whole fruit (bagged)	0	<0.05
								5	<0.05
								10	<0.05
								15	0.13
								25	<0.05
							Pulp (bagged)	0	<0.05
								5	<0.05
								10	<0.05
								15	<0.05
								25	<0.05
RNC 95160 La Aguja, Colombia, 1996	88 OL	Ground	0.56	20	2.8	4	Whole fruit (unbagged)	0	0.12
			0.52	20	2.6			5	0.07
			0.57	20	2.9		Pulp (unbagged)	0	<0.05
			0.53	20	2.7			5	<0.05
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	<0.05
								5	<0.05
RNC 95161 Batan, Honduras, 1996	88 OL	Ground	0.53	20	2.65	4	Whole fruit (unbagged)	0	0.47
			0.50	20	2.5			5	0.65
			0.50	20	2.5		Pulp (unbagged)	0	0.19
			0.54	20	2.7			5	0.28
							Whole fruit (bagged)	0	<0.05
								5	<0.05

Report No., Location, Country, Year	Form.	Type of application	Application rate			No. of treat-ments	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
							Pulp (bagged)	0	<0.05
								5	<0.05
RNC 95162 Cortes, Honduras, 1996	88 OL	Ground	0.54	20	2.7	4	Whole fruit (unbagged)	0	0.30
			0.52	20	2.6			5	0.43
			0.54	20	2.7		Pulp (unbagged)	0	0.14
			0.48	20	2.4			5	0.12
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	<0.05
								5	<0.05
RNC 95163 San Marcos, Guatemala, 1996	88 OL	Ground	0.62	20	3.1	4	Whole fruit (unbagged)	0	0.70
			0.53	20	2.7			5	0.45
			0.57	20	2.9		Pulp (unbagged)	0	0.18
			0.56	20	2.8			5	0.12
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	<0.05
								5	<0.05
RNC 95164 Chiapas, Mexico, 1996	88 OL	Ground	0.58	20	2.9	4	Whole fruit (unbagged)	0	0.32
			0.57	20	2.9			5	0.18
			0.52	20	2.6		Pulp (unbagged)	0	0.07
			0.49	20	2.5			5	0.08
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	NA[1]
								5	<0.05
RNC 95168 Pueblo Nuevo, Costa Rica, 1996	88 OL	Aerial	0.61	20	3.1	4	Whole fruit (unbagged)	0	0.11
			0.57	20	2.9			5	0.09
			0.57	20	2.9		Pulp (unbagged)	0	<0.05
			0.52	20	2.6			5	<0.05
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	NA
								5	<0.05
RNC 95169 Boliche, Ecuador, 1996	88 OL	Aerial	0.52	20	2.6	4	Whole fruit (unbagged)	0	<0.05
			0.54	20	2.7			5	<0.05
			0.54	20	2.7		Pulp (unbagged)	0	NA
			0.60	20	3.0			5	NA
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	NA
								5	NA
RNC 95170 Cienaga, Colombia, 1996	88 OL	Aerial	0.55	20	2.75	4	Whole fruit (unbagged)	0	<0.05
			0.56	20	2.8			5	<0.05
			0.58	20	2.9		Pulp (unbagged)	0	<0.05
			0.54	20	2.7			5	<0.05
							Whole fruit (bagged)	0	<0.05
								5	<0.05
							Pulp (bagged)	0	<0.05
								5	NA
95/10747, trial 1	75 EC	Simulated	0.53	20	2.6	4	Whole fruit	0	<0.05

Report No., Location, Country, Year	Form.	Type of application	Application rate			No. of treat-ments	Sample	PHI, days	Residues, mg/kg
			kg ai/ha	Water, l/ha	kg ai/hl				
Lareinty, Martinique, Lesser Antilles, 1994		aerial treatment				(dry season)	(bagged)	3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 2 Petit Morne, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (dry season)	Whole fruit (bagged)	0	0.07
								3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 3 Rivière Lézarde, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (dry season)	Whole fruit (bagged)	0	<0.05
								3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 4 Rivière Lézarde, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (dry season)	Whole fruit (bagged)	0	<0.05
								3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 5 Rivière Lézarde, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (wet season)	Whole fruit (bagged)	0	<0.05
								3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 6 Rivière Lézarde, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (wet season)	Whole fruit (bagged)	0	0.13
								3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 7 Bochet, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (wet season)	Whole fruit (bagged)	0	<0.05
								3	<0.05
								7	<0.05
								14	<0.05
95/10747, trial 8 Bochet, Martinique, Lesser Antilles, 1994	75 EC	Simulated aerial treatment	0.53	20	2.6	4 (wet season)	Whole fruit (bagged)	0	<0.05
								3	<0.05
								7	<0.05
								14	<0.05

[1] NA: not analysed

In animals

Cattle (Tribolet, 1999). Eleven lactating Simmental x Red Holstein crossbreed cows (9 treated and 2 controls) were selected from 15 animals 10 days before the first treatment on the basis of milk production, general health and body weight.

The nominal doses were 150, 450 and 1500 mg fenpropimorph/animal/day. The cows were fed with 26 kg of maize silage daily and the measured dose rates were 136, 408 and 1363 mg/animal/day giving levels of 5.2, 15.7 and 52.4 ppm of fenpropimorph in the daily feed. The

calculated daily dose rates per kg body weight based on an average body weight of 600 kg were 0.23, 0.68 and 2.3 mg fenpropimorph. The cows were dosed daily for at least 28 days.

Samples of tissues, fat and blood were analysed for fenpropimorph acid (BF 421-2) only. The results are given in Table 12. The results are not corrected for recoveries: the controls were all below the LODs (0.01 mg/kg for muscle, fat and kidney, 0.1 mg/kg for liver and 0.05 mg/l for blood). The average residues of BF 421-2 found in muscle (tenderloin, round steak and diaphragm) of the low, middle and high dose groups were 0.03, 0.03 and 0.19 mg/kg. The corresponding residues in the other samples were 0.09, 0.10 and 0.73 mg/kg in kidneys, 0.75, 0.57 and 5.6 mg/kg in liver, 0.02, 0.02 and 0.15 mg/kg in fat (omental and perirenal, and 0.13, 0.15 and 1.1 mg/kg in blood. There was no significant difference between the mean residues of BF 421-2 in the muscle, liver, kidney, fat and blood from the two lower dose groups. The residues from the highest dose group were between about 6 and 8 times those from the lowest, so slightly less than proportional to the dose.

Table 12. Residues of BF 421-2 in tissues, fat and blood (Tribolet, 1999).

Dose, ppm	Cow no.	Residues, mg/kg							mg/l
		Tenderloin muscle	Round steak	Diaphragm muscle	Liver	Kidney	Perirenal fat	Omental fat	Blood
0	229	<0.01	<0.01	<0.01	<0.1	<0.01	<0.01	<0.01	<0.05
5	220	0.03	<0.01	0.03	0.56	0.08	0.02	0.02	0.12
	222	0.02	0.03	0.04	0.75	0.11	0.02	0.02	0.15
	227	0.04	0.01	0.04	0.94	0.08	0.02	0.02	0.13
	Mean	0.03[2]			0.75	0.09	0.02[3]		0.13
15	221	0.02	0.03	0.03	0.45	0.10	0.02	0.02	0.14
	224	0.02	0.02	0.02	0.51	0.08	0.02	0.01	0.16
	234	0.04	0.02	0.03	0.74	0.12	0.03	0.03	0.16
	Mean	0.03[2]			0.57	0.10	0.02[3]		0.15
50	223	0.21/0.19[1]	0.22/0.19	0.25/0.25	8.6/7.0	0.92	0.18	0.12	0.94
	225	0.09/0.10	0.09/0.08	0.10/0.09	4.1/3.0	0.34	0.08	0.07	0.61
	230	0.31/0.31	0.24/0.26	0.26/0.26	6.2/4.8	0.92	0.22	0.22	1.72
	Mean	0.19[2]			5.6	0.73	0.15[3]		1.09

[1]The two values for each cow are the results of analyses with and without a further clean-up step respectively.
[2]Average of all results for tenderloin, round steak and diaphragm
[3]Average of all residues in perirenal and omental fat

Milk was analysed for BF 421-2 with the results shown in Table 13. The results were not corrected for recoveries, and all the residues in the control samples were below the LOD of 0.002 mg/l.

In the two lower dose groups the residues of BF 421-2 in individual animals reached a plateau in about 7 days. The range of the group mean residues from day 7 to day 28 was 0.01-0.013 and 0.015-0.019 mg/l in the 5 ppm and 15 ppm dose groups respectively. In the 50 ppm group the residues reached a plateau after 14 days. The range of the group means from day 14 to day 28 was 0.051 (day 21)- 0.11 (day 14) mg/l. The individual results show substantial variation between animals of the same dose group as well as between sampling dates when the plateau has been reached. There is only a slight difference between the 5 and 15 ppm dose groups. The results for animals 227 and 220 in the 5 ppm dose group are about the same as for the cows in the 15 ppm group until day 17, but lower thereafter.

Table 13. Residues of BF 421-2 in milk (Tribolet, 1999).

Day	BF 421-2, µg/l, individual cows and group means[1,2]									
	Control	5 ppm group			15 ppm group			50 ppm group		
	229	220	222	227	221	234	224	223	225	230
-4	<2/<2	<2/<2	<2/<2	<2/<2	<2/<2	<2/<2	<2/NA[3]	<2/<2	<2/<2	<2/NA
		Mean <2			Mean <2			Mean <2		
-3	<2/<2	<2/<2	<2/<2	<2/<2	<2/<2	<2/<2	<2/NA	<2/<2	<2/<2	<2/NA
		Mean <2			Mean <2			Mean <2		
1	<2/<2	<2/<2	<2/<2	<2/<2	2.0/<2	3.3/2.7	<2/NA	12/17	6.9/6.6	NA/29
		Mean <2			Mean 2			Mean 17		
4	<2/<2	9.2/13	3.9/4.3	5.0/5.0	13/13	11/12	2.7/NA	58/78	32/36	NA/86
		Mean 7			Mean 9			Mean 63		
7	<2/NA	17/22	3.6/4.1	6.0/5.6	20/16	17/18	8.1/NA	50/63	24/32	NA/71
		Mean 10			Mean 15			Mean 52		
9	<2/<2	12/15	4.1/4.6	15/16	12/12	15/18	16/NA	75/75	32/33	NA/66
		Mean 11			Mean 15			Mean 58		
14	<2/<2	19/15	5.3/5.2	15/17	18/15	16/18	24/NA	94/121	41/46	NA/173
		Mean 13			Mean 19			Mean 110		
17	NA/<2	17/NA	6.0/7.2	15/18	12/13	16/20	16/NA	86/100	54/54	NA/129
		Mean 13			Mean 16			Mean 92		
21	<2/<2	8.4/NA	4.9/6.6	16/17	15/18	19/20	17/NA	35,47,50 /67	NA/37	NA/66
		Mean 10			Mean 18			Mean 51		
23	<2/NA	6.1/4.8	4.2/5.2	20/23	16/22	17/18	7.2/NA	101/104	33/43	NA/71
		Mean 11			Mean 15			Mean 71		
28	<2/NA	9.5/8.9	10/13	13/18	9/18	28/29	14/NA	67,68,47 /95	27/46	NA/89
		Mean 12			Mean 19			Mean 65		

[1] Mixture of morning and evening milk analysed
[2] The two values for each cow are the results of analyses with and without a further clean-up step respectively.
The mean of each pair was taken to calculate the group means
[3] NA: not analysed

FATE OF RESIDUES IN STORAGE AND PROCESSING

No new information.

Residues in the edible portion of food commodities

Fenpropimorph residues in banana pulp from bagged and unbagged bananas were <0.05 (7), 0.07, 0.07, 0.08 and 0.2 mg/kg, and <0.05 (4), 0.06, 0.08, 0.14, 0.18, 0.28, 0.29, 0.3 and 0.43 mg/kg, respectively (see Table 11).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed that the national MRL for cereal grains in Poland is 0.5 mg/kg (residue defined as fenpropimorph *per se*).

APPRAISAL

Fenpropimorph was first evaluated for residues by the 1995 JMPR. That Meeting estimated maximum residue levels which were recommended for use as MRLs for cereals (barley, oats, rye, wheat), cereal straw and fodder (dry), sugar beet and fodder beet leaves and tops.

Conventional livestock and poultry feeding studies with determination of fenpropimorph and the main metabolites identified in metabolism studies, and validated analytical regulatory methods (including representative chromatograms) for the determination of fenpropimorph and its main metabolites in animal products were listed as desirable.

A dairy cattle feeding study and an analytical method for animal products as well as information on GAP, a metabolism study and residue data on bananas have been reported to the present Meeting.

Plant metabolism

Banana plants were treated four times at the twofold application rate of 0.9 kg ai/ha with morpholine-2,6-^{14}C- and phenyl-U-^{14}C-labelled fenpropimorph.

On a whole fruit basis, bananas treated with morpholine-labelled fenpropimorph had a maximum TRR as fenpropimorph of about 0.67 mg/kg in unripe, and 0.61 mg/kg in ripe, unbagged fruit. The corresponding values for bagged fruit were 0.35 and 0.32 mg/kg. Bananas treated with the phenyl-labelled compound had significantly lower TRR levels: 0.11 mg/kg (unripe, unbagged) and 0.09 mg/kg (ripe, unbagged). The corresponding values for bagged bananas were 0.025 and 0.026 mg/kg.

Most of the total ^{14}C was extractable with methanol: 83 to 88% from ripe fruit and 27% to 72% from unripe fruit. The extract of bananas treated with the morpholine-labelled compound showed two main HPLC peaks. One was non-polar and identified by MS as unchanged fenpropimorph. The other peak was polar and was identified by HPLC after acetylation as a mixture of natural assimilation products (glucose, fructose, saccharose). Bananas treated with phenyl-labelled fenpropimorph showed only one prominent HPLC peak which was identified as fenpropimorph.

In contrast to the metabolism in cereals (1995 JMPR), the metabolites 4-{3-[4-(2-hydroxy-1,1-dimethyl)ethylphenyl]-2-methylpropyl}-*cis*-2,6-dimethylmorpholine (BF 421-1), 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid (BF 421-2), methyl 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionate (BF 421-2-Me), [3-(4-*tert*-butylphenyl)-2-methylpropyl](2-hydroxypropyl)amine (BF 421-7), *cis*-2,6-dimethylmorpholine (BF 421-

10), 4-[3-(4-*tert*-butylphenyl)-2-methyl-1-oxopropyl]-*cis*-2,6-dimethylmorpholine (BF 421-13) and 4-[3-(4-*tert*-butylphenyl)-2-methyl propyl]-*cis*-2,6-dimethylmorpholin-3-one (BF 421-15) were not reported.

Farm animal metabolism

In goats fenpropimorph acid, BF 421-2, is the main component of the residue. BF 421-2 would not be expected to concentrate in lipid-rich tissues and products, but it can occur at detectable levels. In liver, the data suggested that the residues of BF 421-2 plus its conjugates would almost certainly be no more than twice the level of BF 421-2 alone. In hens BF 421-2 is probably also the main metabolite but, since residues were only characterized in plasma, liver and kidneys, there was no information on the nature of the residue in poultry meat, fat or eggs (1995 JMPR).

Methods of residue analysis

BASF method 241/1 was developed to determine residues of fenpropimorph in bananas. Fenpropimorph was distilled from the fruit using a Bleidner apparatus after mixing with aqueous sodium bicarbonate solution and the distillate was collected in dichloromethane. After clean-up by liquid/liquid partition and a cation-exchange column, the final residues were quantified by GLC with an NPD. The LOD for whole fruit and pulp was 0.05 mg/kg.

The official multi-residue method of analysis in The Netherlands describes the determination of fenpropimorph residues in fatty and non-fatty foods by GLC with an ion trap detector. The LOD is 0.05 mg/kg.

BF 421-2, the main metabolite of fenpropimorph in animal products, is extracted from fat with hexane, from meat liver and kidney by maceration with methanol/aqueous pH 9 buffer, and from milk and eggs with acetonitrile/aqueous pH 9 buffer. After liquid-liquid partition and further clean-up on a C-18 bonded silica gel column, the BF 421-2 is determined by HPLC with a UV detector. LODs are 0.01 mg/kg for animal tissues and eggs, and 0.002 mg/l for milk. No conjugates of BF 421-2, other metabolites or the parent compound are determined by the method.

Under frozen storage, fenpropimorph residues are stable for at least 7.5 months in bananas. Recoveries of BF 421-2 when stored frozen for 7-8 months were muscle 66%, fat 74%, blood 76%, milk 81%, liver 92% and kidney 95%.

Definition of the residue

The 1995 JMPR concluded that for enforcement and dietary intake purposes the residue in plants should be defined as fenpropimorph. No residue definition was proposed for animal products.

The present Meeting agreed that the definition of the residue for compliance with MRLs for plant commodities should be fenpropimorph *per se*. On the basis of the metabolism in bananas, the same definition should be acceptable for the estimation of the dietary intake in bananas.

On the basis of the metabolism studies on rats and lactating goats reviewed by the 1995 JMPR, the Meeting agreed that BF 421-2 can be used as a marker compound for enforcement purposes. The definition of the residue for compliance with MRLs for animal products should therefore be 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid (BF 421-2), expressed as fenpropimorph. The same definition should be used for animal products to estimate the dietary intake.

In view of the residues found in animals in the tissues and organs in the metabolism and feeding studies, the Meeting concluded that BF 421-2 should not be categorised as fat-soluble.

The Meeting concluded that the following residue definitions are appropriate.

Commodities of plant origin for compliance with MRLs and for the estimation of dietary intake: fenpropimorph

Commodities of animal origin for compliance with MRLs and for the estimation of dietary intake 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid expressed as fenpropimorph.

Residues resulting from supervised trials

Bananas. Fenpropimorph is registered in Cuba for 4–12 applications of 0.44 kg ai/ha and 2.2 kg ai/hl. In view of the fungicide resistance management strategy for morpholine products, the four applications used in the supervised trials have been considered to be the maximum number of treatments.

Eight supervised trials were conducted in 1994 in Martinique: 4 x 0.53 kg ai/ha (20 l water/ha, 2.6 kg ai/hl) were applied to bagged bananas as a simulated aerial treatment. On day 0, the residues in the whole fruit were <0.05 (6), 0.07 and 0.13 mg/kg.

A further 15 trials were conducted in 1996 in Costa Rica (4), Ecuador (4), Columbia (3), Honduras (2), Guatemala (1) and Mexico (1), all with 4 applications at the nominal application rate of 0.545 kg ai/ha (20 l water/ha, 2.7 kg ai/hl). In each plot 50% of the trees were bagged. Twelve trials were with ground and three with aerial applications. Residues in the ground-sprayed trials on the day of treatment were as follows.

Unbagged bananas, whole fruit: 0.1, 0.12, 0.16, 0.26, 0.32, 0.36, 0.43, 0.65, 0.7, 0.75, 1.2, 1.4 mg/kg
Unbagged bananas, pulp: <0.05 (4), 0.06, 0.08, 0.14, 0.18, 0.28, 0.29, 0.3, 0.43 mg/kg
Bagged bananas, whole fruit: <0.05 (7), 0.13, 0.16, 0.17, 0.33, 0.4 mg/kg
Bagged bananas, pulp: <0.05 (7), 0.07, 0.07, 0.08, 0.2 mg/kg

The residues from aerial application were significantly lower. One sample of unbagged whole fruit contained 0.11 mg/kg. Residues in all the other samples were below the LOD.

The Meeting estimated a maximum residue level of 2 mg/kg based on the residues in ground-sprayed unbagged whole fruit and an STMR of 0.11 mg/kg from the corresponding residues in the pulp.

Animal products. Assuming worst-case feeding situations, the maximum theoretical fenpropimorph levels in animal feed were estimated by the 1995 JMPR to be 1.3 ppm for beef cattle, 1.7 ppm for dairy cattle and 0.35 ppm for poultry.

Groups of 3 cows were fed for 28 days with 26 kg maize silage containing 5.2 ppm, 15.7 ppm or 52.4 ppm fenpropimorph. For an average body weight of 600 kg the calculated daily dose rates were 0.23, 0.68 and 2.3 mg fenpropimorph per kg body weight. Milk samples were collected from all cows on days 1, 4, 7, 9, 14, 17, 21, 23 and 28. At the end of the test period the animals were slaughtered and their tissues and milk analysed for residues of the metabolite BF 421-2.

There was hardly any difference in the residues of BF 421-2 in the milk or tissues between the two lower dose groups. No clear explanation for this was suggested. As the ratios of the high/mean residues in the 52.4 to 5.2 ppm dose group in milk were 8.8/8.3, in liver 9.1/7.5, in kidney 8.4/8.3, in muscle 7.8/6.3 and in fat 11/7.8, indicating near linearity, further calculations assuming a more realistic dietary burden of 1.7 ppm were based on the residues in these groups only. The following

Table shows the highest and the mean measured and extrapolated residues. Since the residues reached a plateau in the milk slowly (in 2 weeks), maximum residue levels were estimated from the highest extrapolated residues. STMRs were estimated from the mean extrapolated residues.

Dose group ppm	BF 421-2 residues, calculated as fenpropimorph, mg/kg									
	Milk, day 14		Liver		Kidney		Muscle		Fat	
	high	mean	high	mean	high	mean	high	mean	high	mean
1 x rate, 5.2 (1.7) [1]	0.017 (0.006)	0.012 (0.004)	0.86 (0.28)	0.68 (0.22)	0.1 (0.033)	0.08 (0.026)	0.036 (0.012)	0.027 (0.009)	0.018 (0.006)	0.018 (0.006)
3 x rate, 15.7 (1.7)	0.022 (0.0024)	0.017 (0.0018)	0.67 (0.073)	0.52 (0.056)	0.11 (0.012)	0.091 (0.01)	0.036 (0.004)	0.027 (0.003)	0.027 (0.003)	0.018 (0.002)
10 x rate, 52.4 (1.7)	0.16 (0.005)	0.1 (0.003)	7.8 (0.25)	5.1 (0.17)	0.84 (0.027)	0.66 (0.021)	0.28 (0.009)	0.17 (0.006)	0.2 (0.006)	0.14 (0.005)

[1]Values in parenthesis: calculated, assuming 1.7 ppm intake

The Meeting estimated maximum residue levels of 0.01 mg/kg for milk, 0.3 mg/kg for liver, 0.05 mg/kg for kidney, 0.02 mg/kg for meat and 0.01 mg/kg for fat and STMR levels of 0.004 mg/kg for milk, 0.22 mg/kg for liver, 0.026 mg/kg for kidney, 0.009 mg/kg for meat and 0.006 mg/kg for fat.

As the metabolism is similar in rats and cows, these levels are estimated for cattle, goats, sheep and pigs.

The Meeting noted that the nature of the residue in poultry meat, fat and eggs is unknown and no feeding study was carried out. Nevertheless, taking into account the results of the poultry metabolism study reviewed by the 1995 JMPR, with doses of 51.5 ppm in the diet with the phenyl label and 39.3 ppm with the morpholine label compared with the low estimated maximum dietary burden of 0.35 ppm, the Meeting concluded that no residues are to be expected in poultry products.

RECOMMENDATIONS

The Meeting estimated the following maximum residue levels which are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and estimation of dietary intake for plant commodities: fenpropimorph.

For compliance with MRLs and estimation of dietary intake for animal commodities: 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid expressed as fenpropimorph.

Commodity		Recommendation		
		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FI 0327	Banana	2		0.11
PE 0112	Eggs	0.01*		0
MO 0098	Kidney of cattle, goats, pigs and sheep	0.05		0.026

Commodity		Recommendation		
		MRL, mg/kg		STMR,
CCN	Name	New	Previous	mg/kg
MO 0099	Liver of cattle, goats, pigs and sheep	0.3		0.22
MF 0100	Mammalian fats (except milk fats)	0.01		0.006
MM 0095	Meat (from mammals other than marine mammals)	0.02		0.009
ML 0106	Milks	0.01		0.004
PF 0111	Poultry fats	0.01*		0
PM 0111	Poultry meat	0.01*		0
PO 0111	Poultry, Edible offal of	0.01*		0

DIETARY RISK ASSESSMENT

Chronic intake

STMRs have been estimated by the current Meeting for bananas and animal products. Where consumption data were available these STMRs were used in the estimates of dietary intake together with the draft MRLs for 5 other food commodities.

The estimated dietary intakes for the five GEMS/Food regional diets, based on these MRLs and STMRs, were in the range of 10-90% of the ADI. The Meeting concluded that the intake of residues of fenpropimorph resulting from its uses that have been considered by the JMPR is unlikely to present a public heath concern.

Acute intake

The international estimate of short-term intake (IESTI) for fenpropimorph was calculated for the only commodity for which an MRL and STMR were established and for which consumption data (large portion consumption and unit weight) were available. The results are shown in Annex IV. The IESTIs were 0.0045 mg/kg bw for the general population and 0.018 mg/kg bw for children. As no acute reference dose has been established, the acute risk assessment for fenpropimorph was not finalized.

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FENPYROXIMATE(193)

EXPLANATION

Fenpyroximate was first evaluated by the 1995 JMPR, which allocated an ADI of 0-0.01 mg/kg bw. The Meeting estimated a maximum residue level of 0.2 mg/kg for apples but this could not be recommended for use as an MRL owing to the lack of critical supporting data.

The manufacturer provided new residue data for oranges, grapes and hops, a feeding study on cows, metabolism studies on goats and rats, and a processing study on apples.

Information on national MRLs and GAP were provided by the governments of Australia, Germany, Poland, The Netherlands and the UK.

Animal metabolism

The 1995 JMPR considered the need for a livestock metabolism study in accordance with FAO guidelines in future submissions. The present Meeting received reports of a goat metabolism study. A poultry metabolism study was not reported because byproducts of citrus, apples, grapes and hops, on which fenpyroximate is used, are not included in poultry feed.

Two lactating goats were dosed orally twice daily for 3 consecutive days by gelatin capsule with either [*pyrazole*-3-^{14}C]fenpyroximate (10 ppm fenpyroximate in the diet = 0.5 mg/kg bw/day) or [U-*benzyl*-^{14}C]fenpyroximate (10 ppm in the diet = 0.3 mg/kg bw/day) (Jalali and Gibson, 1999a,b). The body weights of the goats were 34 and 41 kg, and the feed intakes 1.6 and 1.4 kg animal/day (dry weight). Milk and faeces were sampled twice daily and urine once daily, and the goats were slaughtered approximately 22 hours after the final dose.

The total recovery of radioactivity was 80% for the pyrazole label and 84% for the benzyl label. Excretion in the faeces and urine was found to be a significant route of elimination of fenpyroximate. The recovery of radioactivity from the urine was 32% of the pyrazole label and 12% of the benzyl label. The faeces accounted for 32% of the pyrazole label and 45% of the benzyl label. Less than 0.2% of the dose was excreted in the milk by both goats. The tissues contained small amounts of radioactivity, 3.3% of the total dose from the pyrazole label and 6.0% from the benzyl label. The highest levels of ^{14}C in the tissues were found in the livers and kidneys. The distribution of ^{14}C in the tissues, milk and excreta is shown in Table 1.

Table 1. Distribution of the total radioactive residue (TRR) in the tissues, milk and excreta from lactating goats dosed for 3 consecutive days with either [*pyrazole*-3-^{14}C]fenpyroximate (10 ppm in the diet) or [U-*benzyl*-^{14}C]fenpyroximate (10 ppm in the diet) and slaughtered 22 hours after the final dose (Jalali and Gibson, 1999a,b).

Sample	Pyrazole label		Benzyl label	
	TRR, mg/kg[1]	% of total dose	TRR, mg/kg[1]	% of total dose
Liver	1.2	1.7	1.3	2.7
Kidney	1.1	0.2	2.1	0.7
Muscle	0.021	0.7	0.024	1.1
Fat	0.082	0.6	0.14	1.4

Sample	Pyrazole label		Benzyl label	
	TRR, mg/kg[1]	% of total dose	TRR, mg/kg[1]	% of total dose
Blood	0.026	0.1	0.034	0.1
Milk	0.004-0.033	0.2	0.008-0.031	0.1
Urine	1.1-4.4	25	0.4-1.3	11
Cage wash	0.26	7.3	0.035	1.0
Faeces	0.01-10	31	0.000-11	40
Cage solid	0.48	2	4.3	4.3
Bile	2	0.1	6.2	<0.1
Gastrointestinal tract	0.64	11	0.87	22
Total	–	79.9	–	84.5

[1] As fenpyroximate

The samples were extracted with hexane, acetonitrile and acetonitrile/water. The liver, kidney and fat samples were then hydrolysized with HCl, NaOH and/or protease. The extracts were analysed by HPLC, TLC and LC-MS.

Over 90% of the ^{14}C was extracted from the liver, kidney and muscle of both goats and from the fat of the goat dosed with the phenyl label; 81% from the fat of the other goat. The radioactivity extracted from the milk ranged from 67% to 96% of the pyrazole label and 85% to 136% of the benzyl label. Metabolism was rapid. Traces of fenpyroximate were found in the fat, kidneys, muscle and milk. Ten metabolites (G-1-G-10) were identified or characterized. The major compounds found were G-4, *(E)-α-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-p-toluic acid* (identified as C in the 1995 evaluation) and G-7 (Y in 1995) *(E)-α-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-p-toluic acid* in the liver and kidneys, G-2 *(1-hydroxylmethyl-1-methylethyl (E)-α-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-p-toluate)* and G-4 in muscle and fat, and fenpyroximate, G-2 and G-9 (S) *(4-cyano-1-methyl-5-phenoxypyrazole-3-carboxylic acid)* in the milk. M-8 (H) *(1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid)* and G-9 (S) were the major components in the urine. The faeces contained fenpyroximate and G-2. The metabolite G-1 (A) is the (*Z*)- stereoisomer of the parent fenpyroximate. The compounds detected in the tissues and milk are shown in Tables 3 and 4.

Metabolites G-4 (C), G-7 (Y) and G-9 (S) were reported in the 1995 monograph to be found in rats. Metabolite G-2 was considered to be an intermediate in the hydrolysis of fenpyroximate to G-4 (C) and was detected in the liver and plasma of rats (Motoba, 1992). It was therefore considered that there were no essential differences between metabolism in rats and goats. The proposed metabolic pathways are shown in Figure 1.

Table 2. Metabolites identified in the tissues and milk of a goat dosed with [*pyrazole*-3-^{14}C]fenpyroximate (10 ppm in the diet) for 3 days and slaughtered 22 hours after the final dose (Jalali and Gibson, 1999a).

Sample	^{14}C expressed as fenpyroximate, mg/kg									
	TRR	Fenpyro-ximate	G-1 (A)	G-2	G-3 (T)	G-4 (C)	G-7 (Y)	G-9 (S)	G-6	G-10
Liver	1.21	<0.001	<0.001	0.042	0.053	0.609	0.265	0.016	0.023	0.042
Kidney	1.10	0.005	<0.001	0.016	0.094	0.462	0.305	0.023	0.050	0.044
Muscle	0.024	0.006	<0.001	0.014	<0.001	0.002	<0.001	<0.001	<0.001	<0.001
Fat	0.082	0.035	<0.001	0.029	<0.001	0.006	<0.001	<0.001	<0.001	<0.001

Sample	^{14}C expressed as fenpyroximate, mg/kg									
	TRR	Fenpyro-ximate	G-1 (A)	G-2	G-3 (T)	G-4 (C)	G-7 (Y)	G-9 (S)	G-6	G-10
Milk 0-8hr	0.004									
8-24hr	0.020	0.001	<0.001	<0.001	<0.001	<0.001	<0.001	0.011	<0.001	<0.001
24-32hr	0.026	0.005	<0.001	0.003	<0.001	<0.001	<0.001	0.011	<0.001	<0.001
32-48hr	0.028	0.003	<0.001	0.002	<0.001	<0.001	<0.001	0.010	<0.001	<0.001
48-56hr	0.033	0.008	<0.001	0.003	<0.001	<0.001	<0.001	0.015	<0.001	<0.001
56hr-	0.030	0.001	0.001	0.001	<0.001	<0.001	<0.001	0.011	<0.001	<0.001

Table 3. Metabolites identified in the tissues and milk of a goat dosed with [U-*benzyl*-^{14}C]fenpyroximate (10 ppm in the diet) for 3 days and slaughtered 22 hours after the final dose (Jalali and Gibson, 1999b).

Sample		^{14}C expressed as fenpyroximate, mg/kg								
	TRR	Fenpyro-ximate	G-1 (A)	G-2	G-3 (T)	G-4 (C)	G-7 (Y)	G-6	G-5 (E)	G-8
Liver	1.25	<0.001	0.070	0.068	0.073	0.74	0.25	<0.001	0.036	0.014
Kidney	2.08	0.022	<0.001	0.054	0.140	0.98	0.55	0.10	0.11	0.060
Muscle	0.024	0.002	<0.001	0.020	<0.001	0.009	<0.001	<0.001	<0.001	<0.001
Fat	0.14	0.049	<0.001	0.024	<0.001	0.019	0.003	<0.001	<0.001	<0.001
Milk 0-8hr	0.008									
8-24hr	0.013	0.003	0.005	0.003	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
24-32hr	0.024	0.006	<0.001	0.006	<0.001	0.002	<0.001	<0.001	<0.001	<0.001
32-48hr	0.025	0.004	<0.001	0.004	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
48-56hr	0.031	0.008	<0.001	0.007	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001
56hr-	0.022	0.003	<0.001	0.006	<0.001	<0.001	<0.001	<0.001	<0.001	<0.001

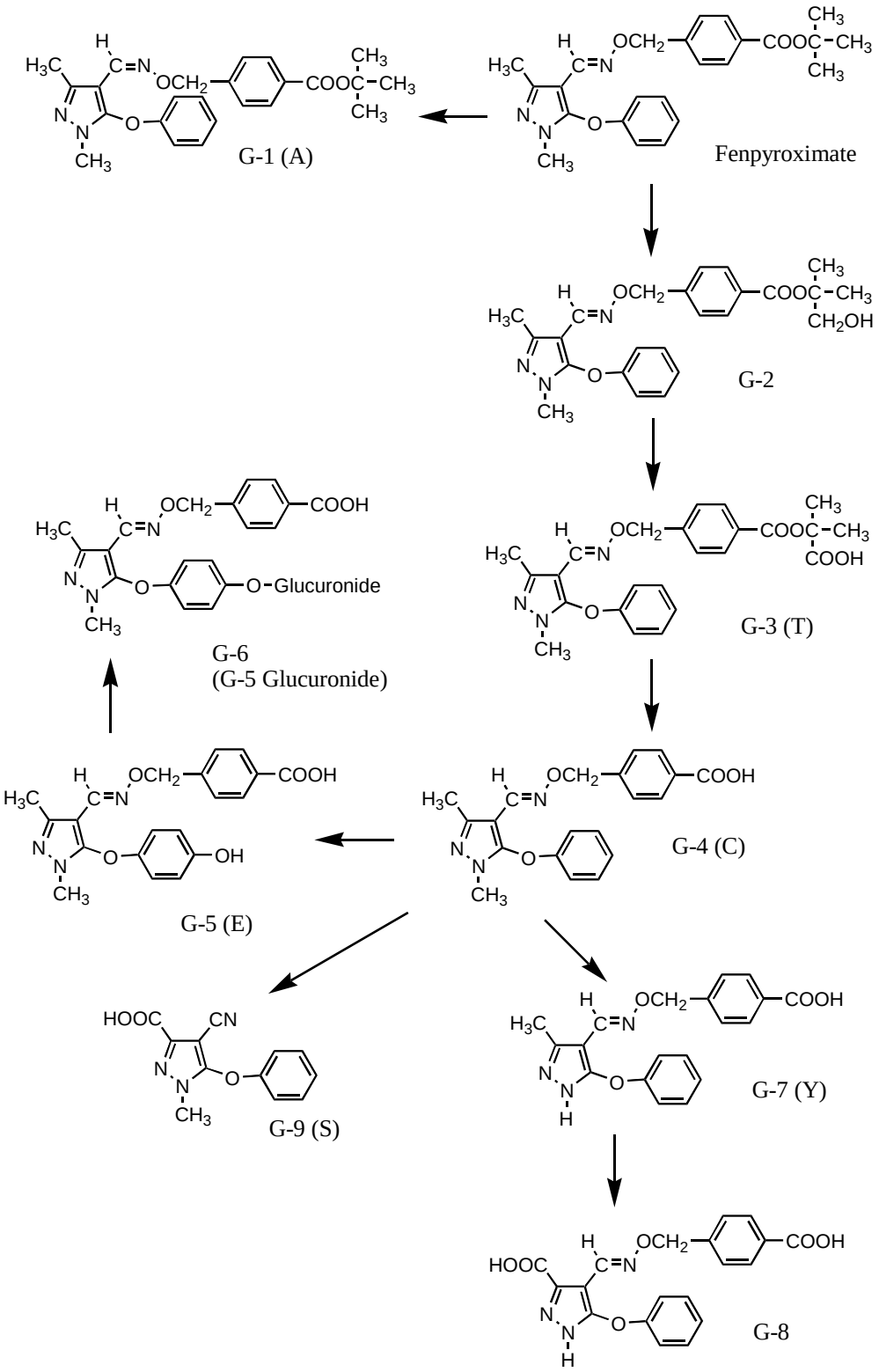
METHODS OF RESIDUE ANALYSIS

Analytical method

The Meeting received information on methods of analysis for fenpyroximate in crops, processed commodities, meat and milk.

A method was developed to determine residues of fenpyroximate in orange pulp, orange peel, grapes, and fresh and dried hops in supervised trials (Todd, 1999).

Figure 1. Proposed metabolic pathways of fenpyroximate in goats.



Oranges and grapes. Homogenized sub-samples of orange pulp, orange peel or grapes are extracted twice with acetone/water and centrifuged. The supernatants are collected and adjusted to a volume with acetone/water. An aliquot of the extract is partitioned with dichloromethane (oranges) or ethyl acetate (grapes) after the addition of sodium chloride. The organic layer is collected and the solvent evaporated. The residue is dissolved in diethyl ether/hexane (1:19) and cleaned up on a silica solid phase extraction (SPE) cartridge, eluting with acetone/hexane (1:1). The eluate is reconstituted in acetonitrile/water (7:3) for quantification by LC-MS.

The method was validated over the range of 0.01-0.5 mg/kg for orange pulp and grapes and 0.05-1.0 mg/kg for orange peel. The recoveries from orange pulp, orange peel and grapes were 80-100%, 81-92% and 78-106% respectively, with LODs of 0.01, 0.05 and 0.01 mg/kg respectively (Table 4).

Hops. Sub-samples of dried hops are homogenized twice with ethyl acetate and water, and centrifuged to separate the phases. The organic phases are collected and the solvent evaporated. The residue is dissolved in methanol and an aliquot is partitioned twice with 2,2,4-trimethylpentane with water and saturated sodium carbonate solution. The organic layer is collected and the solvent evaporated. The residue is dissolved in acetonitrile/water (3:10) and cleaned up on a C-18 SPE cartridge, eluting with acetonitrile. The eluate is reconstituted in acetone/water (7:3) for quantification by LC-MS.

The method was validated over the range of 0.05-1.0 mg/kg, giving recoveries of fenpyroximate of 82-96%, with an LOD in dried hops of 0.05 mg/kg (Table 4).

Table 4. Recoveries and limits of determination of fenpyroximate.

Sample	Fortification level, mg/kg	Recovery, %	Mean recovery, %	SD, %	Limit of quantification, mg/kg
Orange pulp	0.01	100, 97, 80	94	7.0	0.01
	0.05	100, 100, 93			
	0.5	92, 97, 86			
Orange peel	0.05	81, 84, 88	87	3.4	0.05
	0.25	86, 86, 85			
	1.0	92, 91, 88			
Grapes	0.01	78, 79, 87	90	11	0.01
	0.05	80, 83, 94			
	0.5	97, 106, 102			
Dried hops	0.05	94, 96, 82	91	4.2	0.05
	0.25	94, 92, 87			
	1.0	89, 90, 91			

In a method for whole apples, apple juice and apple pomace (Hatfield, 1996) homogenized samples were extracted by blending with aqueous ethyl acetate and celite. After filtratration and evaporation nearly to dryness the sample was dissolved in an ethyl acetate/cyclohexane mixture, and cleaned up by GPC. The GPC eluate was further cleaned up by SPE with elution with toluene/acetone(95:5). The eluate was concentrated and analysed by gas chromatography with a mass-selective detector.

The method was validated over the range of 0.05-0.5 mg/kg giving recoveries of fenpyroximate and G-1 of 92-123 % and 82-118% (Table 5). The limits of determination were approximately 0.05 mg/kg for both compounds.

Table 5. Recoveries of fenpyroximate and G-1 from apples (Hatfield, 1996).

Sample	Fortification level, mg/kg	Fenpyroximate recovery, %	Mean recovery, % (SD, %)	G-1 recovery, %	Mean recovery, % (SD, %)
Apple	0.05	98, 116, 95	101 (11) n = 9	82, 106, 117	103 (13) n = 9
	0.25	95, 97, 123		118, 109, 110	
	0.5	92, 102, 90		93, 101, 89	

Milk, muscle, kidney, fat, and liver (Baker *et al.*, 1999). Milk and muscle samples were extracted with acetone and then acetone/water (2:1). The combined extracts were acidified, concentrated to remove acetone, and the aqueous solution extracted with ethyl acetate. The ethyl acetate extract was partitioned with aqueous sodium carbonate. The ethyl acetate fraction contained fenpyroximate and G-2, and the aqueous fraction contained G-4 and G-9. The ethyl acetate fraction was concentrated and the residue extracted with acetonitrile, and the acetonitrile replaced with hexane/diethyl ether (9:1) for clean-up on a silica SPE cartridge, eluting with diethyl ether. Fenpyroximate and G-2 in the eluate were both hydrolyzed to G-4, which was methylated with diazomethane. The reaction solvent was evaporated, the residue was dissolved in hexane/diethyl ether (9:1), cleaned up on a silica SPE cartridge, and eluted with diethyl ether. The eluate was reconstituted in acetone for GLC with an NPD. The aqueous fraction containing G-4 and G-9 was acidified and extracted with ethyl acetate, the analytes were methylated with diazomethane, and the analysis completed as above.

Fat samples were extracted twice with acetone, and the combined extracts concentrated and dissolved in hexane. The hexane solution was partitioned with aqueous sodium carbonate or ammonium hydroxide. The hexane fraction contained fenpyroximate and G-2, and the aqueous fraction contained G-4. The hexane and aqueous fractions were cleaned up and analysed as described for milk and muscle.

Liver and kidney samples were homogenized twice with acetonitrile/water (4:1). An aliquot of the combined supernatant fractions was partitioned with acetic acid and the aqueous fraction extracted with acetonitrile. The acetonitrile contained fenpyroximate, G-3, G-4 and G-7. The two acetonitrile fractions were combined and reconstituted in ethyl acetate. The ethyl acetate solution was cleaned up by gel permeation chromatography and the eluate methylated with diazomethane and reconstituted in acetonitrile for analysis by LC-MS-MS.

The limits of determination in the milk and the tissues were 0.005 and 0.01 mg/kg respectively. All residues were corrected for concurrent recoveries from fortified samples if these were below 100%.

Stability of residues in stored analytical samples

Samples of milk, muscle, liver and kidney were fortified separately with fenpyroximate and appropriate metabolites as identified in the study of metabolism in goats, and stored frozen for periods of 49-79 days. Analytical recoveries from the stored samples were compared with recoveries from freshly fortified samples. Recoveries of fenpyroximate, G-2 and G-9 from milk were 89, 83 and 65% after frozen storage for 73-79 days. Recoveries of fenpyroximate, G-2 and G-4 from muscle were 60, 68 and 47% after storage for 51-56 days. Recoveries of fenpyroximate, G-2 and G-4 from fat were 67, 37 and 54% after storage for 49-54 days. Again the recoveries from unstored samples were low. After 53-55 days frozen storage, recoveries of fenpyroximate, G-7, G-4 and G-3 were 105, 99, 121 and 107% from liver, and 86, 88, 81 and 89% from kidney. The results are shown in Table 6.

Table 6 Recoveries of fenpyroximate and its metabolites from samples fortified at 0.1 mg/kg after frozen storage.

Sample	Storage period, days	Recovery, %											
		Freshly fortified						After storage					
		Fenpyroximate	G-2	G-9	G-3	G-4	G-7	Fenpyroximate	G-2	G-9	G-3	G-4	G-7
Milk	73	90						89					
	77		92						83				
	79			99						65			
Muscle	51	68	72					60	68				
	56					56						47	
Fat	49					60						54	
	54	76	62					67	37				
Liver	53	99			111	106	117	105			107	121	99
Kidney	55	94			93	87	108	86			89	81	88

Definition of the residue

The current definition is "fenpyroximate". In new animal metabolism and feeding studies the metabolite G-4 was found in the liver and kidneys and G-2 was found in muscle, fat and milk. However, since toxicity studies on fenpyroximate would include these metabolites they indicate that the metabolites would have little or no potential for toxicity.

The Meeting concluded that the current residue definition is suitable both for compliance with MRLs and for the estimation of dietary intake.

The octanol-water partition coefficient and the results of the animal feeding studies indicate that fenpyroximate is fat-soluble.

USE PATTERN

The Meeting received updated information on the registered uses of fenpyroximate on selected crops, shown in Table 7.

Table 7. Registered uses of fenpyroximate on citrus fruits, pome fruits, grapes, and hops (5% SC formulation, foliar application). Entries in bold indicate changes from Table 19 of the 1995 JMPR residue evaluation.

Crop	Country	Application			PHI, days
		kg ai/ha	kg ai/hl	No.	
Citrus fruits	Brazil	**0.05-0.12**	**0.005**	**NS** [1]	15
	Chile		0.0025	1	14
	Greece	**0.1-0.2**	0.004-0.005	**NS**	14
	Italy	0.1	0.005	1	**30**
	Japan		0.003-0.005	1	14
	Spain		**0.005-0.0075**	1	14
Pome fruits	Argentina		0.0025-0.0037	1	14
	Belgium		**0.004-0.005** [2]		**7**
	Chile		0.0025	1	21
	Germany	**0.12**	**0.0075**	**1**	**21**
	Malaysia	0.01-0.02	0.005	1	7
	New Zealand	0.05-0.075	0.0025	1	**28**
	Portugal	0.05-0.075	0.005-0.0075	1	14

Crop	Country	Application			PHI, days
		kg ai/ha	kg ai/hl	No.	
	Spain		**0.0075-0.01**	1	7
	Switzerland	**0.075-0.1**	**0.005**	1	21
Apples	**Australia**[3]	**0.075-0.175**	**0.005**	**1**	**14**
	Australia[4]	**0.038-0.088**	**0.0025**	**1**	**14**
	Brazil	0.06	0.005	1	15
	France	0.06-0.08	0.008	1	21
	Germany	0.12	0.0075	1	21
	Greece	0.06-0.11	0.004-0.005	1	7
	Italy	0.075	0.005	1	14
	Japan		0.003-0.005	1	14
	Poland	**0.06-0.08**	**0.006-0.016**	**1-2**	**7**
	Portugal	0.05-0.075	0.005-0.0075	1	**14**
	UK	0.1		1	14
Grapes	Chile		0.0025	1	30
	Germany	0.092-0.123	0.008	1	35
	Italy	0.05	**0.005**	1	**28**
	Japan		0.003-0.005	1	14
	Portugal	**~ 0.075**	**0.005-0.0075**	1	14
	Spain	**~ 0.1**	**0.0075-0.01**	1	14
	Switzerland	**0.1**	**0.005**	1	21
Hops	Germany	0.225-0.263	0.0075	1	21
	Japan		0.005	1	14

[1] Not specified
[2] 0.004 kg ai/hl in summer
[3] Without integrated pest management (IPM)
[4] With IPM

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials in Spain and Italy on oranges and grapes and in Germany on hops. Trials on these commodities and on apples were reviewed by the 1995 JMPR, and the results are reproduced together with new information in Tables 8-11.

Table 8	Oranges
Table 9	Apples
Table 10	Grapes
Table 11	Hops

Fenpyroximate (5% SC) was applied by backpack lance sprayers in trials on oranges in Italy (compressed air) and Spain (motorized). The plots were single rows of 24 to 30 m, and the row spacing was 4.5 to 7 m. Triplicate samples taken from each row were >6 kg (36 fruit in Spain, 48 in Italy) corrected. Samples were separated into peel and pulp in the field, and stored in a freezer for 29 to 49 days in Spain and 23 to 25 days in Italy before analysis.

Grapes were treated by similar sprayers in Italy and Spain. The plot sizes were 3 rows of 15 m, spaced 2.5 to 3 m apart and each field contained one control and two treated plots. Samples >2 kg (>12 bunches) from each row in Spain and 3.7 to 5 kg (>12 bunches) from each row in Italy. The samples were shipped frozen to the analytical laboratories and stored in a freezer for 5 weeks in Spain and 3 weeks in Italy before analysis.

All applications in the trials on hops were made with commercial airblast sprayers towed by tractors. The plots were 6 rows of 20 m, with 3.1 to 3.3 m spacing, and 1 control and 2 treated plots in each field. Samples were >1 kg of fresh and 0.38 to 0.80 kg of dry hops (equivalent to 1.5 to 2.4 kg of fresh). Samples were shipped to the analytical laboratories in dry ice by air. The hops were dried at 63°C in research kilns for 6 h.

Table 8. Residues of fenpyroximate in oranges in supervised trials in Spain and Italy in 1998, and in citrus in trials reviewed by the 1995 JMPR. Residues in replicate field samples from the same plot in each trial are shown separately. Underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Country, Location, (variety)	Form	Application				Sample	PHI, days	Residues, mg/kg		Ref.
		No	kg ai/ha	water l/ha	kg ai/hl			replicates	mean	
Spain, Lepe (Salustiano)	SC	1	0.14	2001	0.007	pulp	14	<0.01(3)	<0.01	Wilson, 1998, NHH092/ 983274
						peel	14	0.17,0.18,0.19	0.18	
						whole	14	0.05,0.05,0.06	<u>0.05</u>	
				2007		pulp		<0.01(3)	<0.01	
						peel		0.15,0.19,0.14	0.16	
						whole		0.04,0.06,0.04	<u>0.05</u>	
Spain, Cantillana (Valencia late)	SC	1	0.14	2006	0.007	pulp	14	<0.01(3)	<0.01	
						peel		0.13,0.14,0.22	0.16	
						whole		0.03,0.03,0.05	<u>0.04</u>	
		1	0.14	2004	0.005	pulp	14	<0.01(3)	<0.01	
						peel		0.19,0.18,0.16	0.18	
						whole		0.05,0.04,0.03	<u>0.04</u>	
Italy, Catania (Tarocco comune)	SC	1	0.1	2000	0.005	pulp	30	<0.01(3)	<0.01	
						peel		0.17,0.13,0.09	0.13	
						whole		0.05,0.04,0.03	<u>0.04</u>	
		1	0.1	2000	0.005	pulp	30	<0.01(3)	<0.01	
						peel		0.13,0.12,0.10	0.12	
						whole		0.04,0.04,0.03	<u>0.04</u>	
Palagonia (Tarocco comune)	SC	1	0.1	2000	0.005	pulp	31	<0.01(3)	<0.01	
						peel		0.10,0.13,0.15	0.13	
						whole		0.04,0.04,0.05	<u>0.04</u>	
		1	0.1	2000	0.005	pulp	31	<0.01(3)	<0.01	
						peel		0.12,0.09,0.13	0.11	
						whole		0.04,0.03,0.05	<u>0.04</u>	

Trials reviewed by 1995 JMPR.

Country, Year, Crop	Application			PHI, days	Fenpyroximate, mg/kg			Ref.
	No.	kg ai/ha	kg ai/hl		Pulp	Peel	Whole	
Brazil, 1989-1990 Oranges	2	0.08	0.005	15	<0.05	0.2		

				30	<0.05	<0.05		R-08
		0.16	0.01	15	<0.05	0.1		R-09
	2							
				30	<0.05	<0.05		
	2	0.18	0.005	16	<0.05	0.38		R-10
				29	<0.05	0.18		
		0.36	0.01	16	0.08	0.73		R-11
						0.85		
				29	<0.05	0.59		
Greece, 1992	1	0.15	0.005	0	<0.01	0.35	0.12	
Oranges				2	<0.01	0.37	0.11	R-12
				9	<0.01	0.3	0.11	
				16	<0.01	0.26	0.09	
				22	<0.01	0.13	0.05	
				28	<0.01	0.18	0.07	
	1	0.31	0.01	0	<0.01	0.31	0.11	R-13
				2	<0.01	0.28	0.12	
				9	<0.01	0.19	0.07	
				16	<0.01	0.24	0.08	
				22	<0.01	0.19	0.07	
				28	<0.01	0.23	0.08	
Italy, 1990	2	0.077	0.0075	21	0.05	0.38		
Oranges				64	<0.05	0.39		R-14
				113	<0.05	0.35		
	2	0.077	0.0075	21	<0.05	0.3		R-15
				63	<0.05	0.26		
				105	<0.05	0.36		
	2	0.077	0.0075	21	0.06	0.54		R-16
				63	<0.05	0.53		
				84	<0.05	0.4		
	2	0.15	0.015	21	0.08	0.73		R-17
				64	<0.05	0.77		
				113	<0.05	0.62		
	2	0.15	0.015	21	<0.05	0.96		R-18
				63	<0.05	0.57		
				105	<0.05	0.71		
				21	0.08	0.83		R-19
				43	<0.05	0.75		
				84	<0.05	0.72		
Italy, 1991	1	0.1	0.006	28	0.01	0.35		R-01
Mandarins					<0.01	0.42		R-03
	1	0.2	0.013	28	0.03	0.78		R-02
					0.03	0.86		R-04
	1	0.1	0.006	0	0.03	0.52		R-05
				5	0.02	0.5		
				10	<0.01	0.36		
				14	<0.01	0.34		
				25	0.02	0.24		
				28	<0.01	0.13		
	1	0.2	0.013	0	0.05	0.45		R-06
				5	0.06	0.63		
				10	0.03	0.57		
				14	0.03	0.83		
				25	0.02	0.59		
				28	0.01	0.59		
Japan, 1989	1	0.25	0.005	7	0.006	0.15	0.028	R-07
					0.006	0.14		
Mandarins,				14	<0.005(2)	0.15	0.026	
						0.14		

Greenhouse				21	0.009(2)	0.08 0.068	0.019	
				30	0.008 0.007	0.17(2)	0.037	
				44	0.007(2)	0.21 0.18	0.04	
	1	0.5	0.005	7	0.027 0.024	0.99 0.96	0.20	
				14	0.023 0.019	0.98 0.97	0.21	
				21	0.01 0.01	0.69 0.66	0.15	
				30	0.01 0.01	0.67 0.65	0.12	
				44	<0.005(2)	0.72 0.68	0.13	

Table 9. Trials on apples reviewed by 1995 JMPR.

Country, Year	Application			PHI, days	Fenpyroximate, mg/kg	Ref.
	No.	kg ai/ha	kg ai/hl			
Australia, 1992	1	0.083	0.005	0 7 14 24	0.09, 0.07, 0.1, 0.13 0.08, 0.10, 0.05, 0.06 0.14, 0.12, 0.08, 0.18 0.06(2), 0.03, 0.17	R-20
	1	0.16	0.01	0 7 14 24	0.34, 0.30, 0.23(2) 0.19, 0.33, 0.29, 0.22 0.19(2), 0.18, 0.17 0.12, 0.19, 0.08(2)	
Belgium, 1991	1	0.090	0.006	7 14 21 28	0.12 0.10 0.08 0.05	R-21
	1	0.18	0.012	7 14 21 28	0.19 0.17 0.14 0.18	
France, 1989	1	0.06	0.006	0 7 14 21 29	0.1 0.08 0.03 0.02 0.03	R-22
	2	0.06		48 53 69	0.05 0.07 0.03	
	2	0.08	0.008	48 53 69	0.08 0.03 0.04	
France, 1990	1	0.08	0.008	0 7 14 20-21 29	0.11, 0.12 0.05, 0.08 0.06, 0.10 0.05, 0.09 0.03, 0.06	R-22
	2	0.06	0.006	24	0.11	
				68	0.05	
	2	0.08	0.008	24 68	0.16 0.07	
	2	0.17	0.006	45	0.08	
	2	0.23-0.24	0.008	45	0.19	

Country, Year	Application			PHI, days	Fenpyroximate, mg/kg	Ref.
	No.	kg ai/ha	kg ai/hl			
France, 1991	1	0.08	0.008	30 50 75 106 120 144	0.03 0.03 <0.02 <0.02 <0.02 <0.02	R-23
Germany, 1989	2	0.1125	0.0075	0 7 14 21	0.1, 0.19 0.12, 0.18 0.11, 0.1 0.1, 0.09	R-24
	2	0.0643-0.0868	0.0075-0.0073	0 7 14 21	0.12 0.12 0.08 0.09, 0.12	
	2	0.1-0.115	0.0075-0.0076	0 7 14 21	0.21 0.19 0.15 0.16	
	2	0.15	0.001	0 7 14 21	0.23, 0.24 0.23 0.24 0.24	R-25
	2	0.095,0.132	0.01	0 7 14 21	0.12 <0.01(2) 0.12 0.12	
Germany, 1990	1	0.064	0.0075	0 7 14 28 42 56 70 81	0.15 0.11 0.16 0.12 0.09 0.06 <0.05 <0.05	R-26
				92	<0.05	
	1	0.1125	0.0075	0 7 14 28 42 56 70 84 91	0.13 0.14 0.11 0.08 0.06 <0.05 <0.05 <0.05 <0.05	
	2	0.075	0.0075	0 7 14 21 28	0.13 0.08 0.08 0.06 <0.05	
	2	0.081	0.0075	0 7 14 21 28	0.24 0.21 0.18 0.15 0.13	

Country, Year	Application			PHI, days	Fenpyroximate, mg/kg	Ref.
	No.	kg ai/ha	kg ai/hl			
	2	0.1125	0.0075	0 7 14 21 28	0.21 0.17 0.13 0.08 0.11	
	2	0.114	0.0076	0 7 14 21 28	0.05 <0.05 <0.05 <0.05 <0.05	
Japan, 1990	1	0.14	0.005	15 30 45 60	0.11 0.08 0.034 0.042	R-28
	1	0.25	0.005	15 30 45 60	0.048 0.028 0.007 <0.005	
New Zealand, 1991/92	1		0.0025 (3 trials)	7-9 14 28 42-43	0.07, 0.09, 0.12 0.12, 0.13, 0.03 <0.01(3) <0.01(2), 0.01	R-29
	1		0.005 (3 trials)	7-9 14 21 28 42-43 52-56	0.1, 0.07, 0.06 0.05, 0.04, 0.02 <0.01 0.03(2) ,<0.01 <0.01(2), 0.01 <0.01(3)	
New Zealand, 1993/94	1		0.0025 (4 trials)	7-9 14 21 28 35 42-43 49 52-56	0.05, 0.06, 0.01(2) 0.03(2), <0.01, 0.04 0.04(2), 0.02, <0.01 0.03, 0.02, <0.01(2) 0.02(2), 0.01, <0.01 0.02(3), <0.01 0.02, 0.01, <0.01 0.01, <0.01(2)	R-30
	1		0.005 (4 trials)	7-9 14 21 28 35 42-43 49 52-56	0.11, 0.07, 0.06, 0.05 0.08, 0.06(2), 0.03 0.03, 0.04, 0.05, 0.06 0.03(2), 0.05, 0.02 0.03(2), 0.04, 0.01 0.04, 0.03(2), <0.01 0.03, 0.02, 0.01 0.03, 0.01, <0.01	

Table 10. Residues of fenpyroximate in grapes from supervised trials in Spain and Italy in 1998 (Wilson, 1999a), and in trials reviewed by the 1995 JMPR. Residues in replicate field samples from the same plot in each trial are shown separately. Underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Country,	Form.	Application	PHI	Residues	Ref.

		No.	kg ai/ha	Water, l/ha	kg ai/hl	days	mg/kg	
Spain, Bollullos (Cardinal)	SC	1	0.10	991 1007	0.01	14	0.04 0.06	Wilson, 1999a, NHH093/985072
Spain, Los Palacios (Cardinal)	SC	1	0.10	1014 1029	0.01	14	0.04 0.04	
Italy, Granieri (Italia)	SC	1	0.05	1014 1002	0.005	28	0.04 0.02	
Italy, Mazzarrone (Italia)	SC	1	0.05	999 1002	0.005	28	0.04 0.03	

Trials reviewed by 1995 JMPR

Country, Year Location	Application			PHI	Fenpyroximate	Ref.
	No.	kg ai/ha	kg ai/hl	days	mg/kg	
France, 1989	1	0.06	0.006	0	0.05	
				7	<0.02	R-31
				14	<0.02	
				21	<0.02	
				29	<0.02	
	2		0.006	36	0.05	
				37	0.07	R-31
				47	<0.02	
France, 1990	2	0.06	0.006	42	0.05	
				46	0.07	R-31
				55	0.06	
France, 1990	1	0.08	0.008	0	0.1	
				7	0.05	R-31
				14	0.05	
				21	0.08	
				30	0.07	
France, 1989	2	0.08	0.008	36	<0.02	
				37	0.14	R-31
				47	<0.02	
France, 1990	2	0.08	0.008	42	0.08	
				46	0.05	R-31
				55	0.04	
Germany, 1989 Mussbach	2	0.14	0.023	0	0.17	
				7	0.12	R-32
				14	0.11	
				28	0.09	
				35	0.06	
Germany, 1989 Kappelrodeck	2	0.14	0.023	0	0.41	
				7	0.41	R-33
				14	0.27, 0.34	
				28	0.32	
				35	0.4	
Germany, 1989 Pfeddersheim	2	0.18	0.03	0	0.2	
				7	0.12, 0.17	R-34
				14	0.14	
				28	0.21	
				35	0.15	
Willsbach	2	0.18	0.03	0	0.19(2)	
				7	0.18	R-35
				14	0.24	
				28	0.16	

Country, Year Location	Application No.	kg ai/ha	kg ai/hl	PHI days	Fenpyroximate mg/kg	Ref.
				35	0.13, 0.14	
Germany, 1989 Mussbach	2	0.18	0.03	0 7 14 28 35	0.26 0.16 0.1(2) 0.13 0.13	R-36
Germany, 1989 Kappelrodeck	2	0.18	0.03	0 7 14 28 35	0.29 0.3(2) 0.18 0.12 0.16	R-37
Germany, 1991 Nittel	2	0.045-0.035	0.015-0.225	0 7 14 28 35	0.22 0.16 0.16 0.1 0.08	R-38
Muhlhofan	2	0.045-0.135	0.015-0.225	0 7 14 28 35	0.36 0.29 0.17 0.12 0.11	
Italy, 1991	1 1 1 1 1 1	0.081 0.16 0.094 0.19 0.064 0.13	0.0062 0.012 0.0063 0.013 0.0064 0.013	14 14 14 4 14 14	0.47 0.57 0.17 0.52 0.07 0.19	R-39 R-40 R-41
Japan, 1988	1	0.2	0.005	14 21	0.38, 0.41 0.45, 0.41	R-42
greenhouse				30 60	0.36, 0.33 0.062, 0.058	
Japan, 1989 greenhouse	1 2	0.2	0.005 0.005	13 20 29 13 20	0.43(2) 0.53, 0.5 0.51, 0.49 1.1, 1.2 1.1, 1.2	R-43 R-43

Table 11. Residues of fenpyroximate in hops from supervised trials in Germany in 1998 (Wilson, 1999b), and in trials reviewed by the 1995 JMPR. Residues in replicate field samples from the same plot in each trial are shown separately. Underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Country, Year Location	Form.	Application No.	kg ai/ha	water, l/ha	kg ai/hl	Sample	PHI, days	Residues, mg/kg	Report
Germany, Wolnzach (Perle)	SC	1	0.27 0.26	3526 3431	0.008	fresh	21	1.6 1.9	Wilson, 1999b. NHH094/98 4984
						dry	21	4.4 5.0	
Germany, Wolnzach (Magnum)	SC	1	0.28 0.28	3677 3641	0.008	Fresh	21	1.7 1.8	
						dry	21	5.9 8.4	
Germany,	SC	1	0.26	3446	0.008	fresh	21	1.9	

Wolnzach (Hersbrucker)			0.27	3542				1.9	
						dry	21	7.4 6.2	

Trials on hops reviewed by the 1995 JMPR

Country, Year Location	Application			PHI, days	Sample	Fenpyroximate, mg/kg	Ref.
	No.	kg ai/ha	kg ai/hl				
Germany, 1989, Gambach	1	0.375	0.0125	0 7 14 21 21	green dry	5.2, 7.6 1.6, 3.8 0.9, 3.1 0.8, 3.2 6.4, <1	R-44,R-45
Oberrunseried	1	0.375	0.0086	0 7 14 21 21	green dry	2.7, 2.6 1.6, 1.1 1.5, 1.1 0.5, 0.8 2.1, 2.1	R-46,R-47
Germany, 1990, Gambach	1	0.375	0.0188	0 7 14 21 21	green dry	3.1, 1.8 3.7, 2.1 3.7, 2.5 1.1, <0.5 6.8, 8.2	R-48
Germany, 1990, Gambach	1	0.75	0.0375	0 7 14 21	green	11.6 11.3 15.8 10.4	R-48
				21	dry	28.7	
Germany, 1990, Tannant Red	1	0.375	0.015	0 7 14 21 21	green dry	5.3 2.5 2.4 2.1 7.0	R-48
Germany, 1990, Lindau-Bodenegg	1	0.375	0.0094	0 7 14 21 21	green dry	4.7 3.5 13.7 4.9 <1	R-48
Germany, 1990, Lindau-Bodenegg	1	0.75	0.0188	0 7 14 21 21	green dry	25.9 24.1 12.1 9.2 25	
Germany, 1991	1	0.23	0.0075	0 7 14 21 21	green dry	11.3, 6.6, <0.5 1.5, 2.3, 2.6 <0.5, 1.2, 1.7 <0.5, 0.7, 1.6 1.2, 3.7, 4.3	R-49
Germany, 1991	1	0.46	0.015	0 7 14 21 21	green dry	9.8, 6.8, 14.7 4.2, 4.0, 4.0 1.3, 2.5, 2.3 0.6, 1.5, 3.1 2.5, 4.9, 3.6	

Livestock feeding trials

The Meeting received information on a lactating dairy cow feeding study on fenpyroximate. (Baker, 1999)

Three groups of three Holstein dairy cows were dosed orally by gelatin capsules once daily for 29 consecutive days with fenpyroximate at rates equivalent to approximately 1, 3, and 10 ppm dry weight in the diet (19, 57 and 190 mg of fenpyroximate per cow per day). There was one control cow. Milk was collected in the morning and evening on days 0, 1, 3, 7, 11, 14, 18, 21, 24 and 28 and stored frozen until analysis. All the cows were slaughtered between 15 and 22 hours after their final doses and samples of liver (~1 kg), both kidneys, composite round and loin muscle (~1 kg), and composite omental and permental fat (~1 kg) were collected. Tissue samples were homogenized frozen and stored frozen up to 63 days before extraction and analysis. Milk samples were stored frozen for a maximum of 82 days between collection and extraction. The cows were fed a combination of roughage (hay) and high-protein dairy concentrate. In the acclimatization day all the cows were fed 18.7-18.9 kg/day (6.4 kg concentrate and 12.3-12.5 kg hay). During the dosing period the mean feed consumption was 18.7 kg/day for the control cow and 18.9, 19.0 and 19.0 for the 1 ppm, 3 ppm and 10 ppm dose groups. There was little change in the body weights between acclimatization and slaughter. The control cow lost 3 kg, the low-dose group lost a mean 1 kg, the 3 ppm group gained 8 kg and the high-dose group gained 7 kg.

The residues found in the 10 ppm, 3 ppm and 1 ppm dose groups are shown in Tables 13, 14 and 15 respectively.

Milk. The mean residues of fenpyroximate plus G-2 in the 10 ppm dose group reached a maximum of 0.017 mg/kg 1 day after the first dose (the highest individual residue was 0.022 mg/kg after 3 days) and then generally decreased except for a residue of 0.016 mg/kg at 21 days. Residues of G-9 in the 10 ppm group were below the LOD until 24 days and were then 0.005 mg/kg. Milk from the 3 ppm dose group was analysed at 3, 14 and 21 days and contained <0.005-0.011 mg/kg of fenpyroximate plus G-2; residues of G-9 were either not detected or less than 0.005 mg/kg. It was considered that the analyses of milk from the 1 ppm dose group were not necessary.

Muscle. The mean residues in muscle of fenpyroximate plus G-2 in the 10 ppm, 3 ppm and 1 ppm dose groups were 0.038, 0.015 and <0.01 mg/kg respectively (the range was <0.01 to 0.049 mg/kg). The residues of G-4 in the 10 ppm and 3 ppm dose groups were either not detected or less than 0.01 mg/kg.

Fat. The mean residues of fenpyroximate plus G-2 in the 10 ppm, 3 ppm and 1 ppm dose groups were 0.1, 0.056 and 0.015 mg/kg respectively, with a range of 0.01 to 0.16 mg/kg. Residues of G-4 in the 10 ppm and 3 ppm dose groups were all less than 0.01 mg/kg .

Liver. The mean residues of G-4 in the 10 ppm, 3 ppm and 1 ppm dose groups were 0.80, 0.37 and 0.19 mg/kg respectively. Residues of fenpyroximate plus G-2, G-7 and G-3 were ≤0.01 mg/kg in the 10 ppm dose group and not detected in the other groups.

Kidneys. The mean residues of fenpyroximate plus G-2 were 0.014 mg/kg in the 10 ppm dose group, <0.01 mg/kg in the 3 ppm dose group and undetected in the 1 ppm dose group. The mean residues of G-4 were 0.40, 0.29 and 0.20 mg/kg. G-7 and G-3 were undetectable in all three groups.

Table 12. Residues in the milk and tissues of cows dosed at 10 ppm.

Sample	Residues, mg/kg				
	Fenpyroximate/G-2	G-9	G-4	G-7	G-3
Milk/ Day 0	ND, <0.005(2)	ND, <0.005(2)	–	–	–
Day 1	0.017, 0.014, 0.021	ND(3)	–	–	–

Sample	Residues, mg/kg				
	Fenpyroximate/G-2	G-9	G-4	G-7	G-3
Day 3	0.022, 0.015, 0.014	ND(3)	–	–	–
Day 7	0.007, 0.019, 0.015	ND(2), <0.005	–	–	–
Day 11	0.010(2), 0.017	ND(3)	–	–	–
Day 14	0.012(2), 0.014	ND(3)	–	–	–
Day 18	0.007, 0.013, 0.014	ND(2), <0.005	–	–	–
Day 21	0.013, 0.019, 0.015	<0.005(2), ND	–	–	–
Day 24	0.006, 0.007, 0.008	0.005(3)	–	–	–
Day 28	0.015, 0.008, 0.007	<0.005(3)	–	–	–
Liver	<0.010(2), 0.011	–	0.90, 0.70, 0.80	ND(2), <0.01	<0.01, ND(2)
Kidney	0.009, 0.014, 0.019	–	0.35, 0.44, 0.41	ND(3)	ND(3)
Muscle	0.024, 0.040, 0.049	–	ND(2), <0.010	–	–
Fat	0.046, 0.136, 0.12 (0.052, 0.115, 0.159)	–	ND(2), <0.01 (<0.01(3))	–	–

–: not determined ND: not detected

Values in parentheses are from analysis of a second set of samples

Table 13. Residues in the milk and tissues of cows dosed at 3 ppm.

Sample	Residues, mg/kg				
	Fenpyroximate/G-2	G-9	G-4	G-7	G-3
Milk/ Day 3	<0.005(3)	ND(3)	–	–	–
Day 14	0.007, 0.006, 0.011	<0.005(2)	–	–	–
Day 21	0.007, 0.005, <0.005	<0.005(2), ND	–	–	–
Liver	ND(3)	–	0.42(2), 0.28	ND(3)	ND(3)
Kidney	ND(2), <0.01	–	0.35, 0.29, 0.23	ND(3)	ND(3)
Muscle	0.012, 0.017, 0.015	–	ND(3)	–	–
Fat	0.025, 0.073, 0.071	–	ND, 0.01(2)	–	–

–: not determined. ND: not detected

Table 14. Residues in the tissues of cows dosed at 1 ppm.

Sample	Residues, mg/kg				
	Fenpyroximate/G-2	G-9	G-4	G-7	G-3
Liver	ND(3)	–	0.2, 0.16, 0.22	ND(3)	ND(3)
Kidney	ND(3)	–	0.18, 0.23, 0.2	ND(3)	ND(3)
Muscle	<0.01(3)	–	–	–	–
Fat	0.018, 0.016, 0.01	–	–	–	–

–: not determined.

FATE OF RESIDUES IN STORAGE AND PROCESSING

Processing

Apples. In four field trials apples were sprayed twice 21 ± 1 days and 7 days before maturity, at 0.15 kg ai/ha (0.008 kg ai/hl) before maturity. The apples were processed to juice and pomace at A.C.D.S. Research Inc. by procedures that simulated commercial processing.

Fresh, unwashed apples were ground in a hammer-mill and the resulting wet mash was pressed to 155-211 kg/cm^2 for five minutes in one or more cloth stacks in a hydraulic press. The wet pomace remained as a cake after juice extraction. The residues, and the processing factors for pomace, are shown in Table 15. Processing factors could not be calculated for juice because all the residues were below the LOD.

Table 15. Residues of fenpyroximate and G-1 in apples and their processed fractions, USA, 1994.

Location	Fresh apples		Juice		Wet pomace			
	Fenpyroximate, mg/kg	G-1, mg/kg	Fenpyroximate, mg/kg	G-1, mg/kg	Fenpyroximate		G-1	
					mg/kg	PF[1]	mg/kg	PF[1]
MI	0.21, 0.15	<0.05(2)	<0.05	<0.05	0.93	5.17	0.07	1.4
NY	0.10, 0.15	<0.05(2)	<0.05	<0.05	0.65	5.20	<0.05	-
PA	0.06, 0.10	<0.05(2)	<0.05	<0.05	0.48	6.0	<0.05	-
WA	0.10, 0.09	<0.05(2)	<0.05	<0.05	0.38	4.0	<0.05	-

[1] Processing factor

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information.

NATIONAL MAXIMUM RESIDUE LIMITS

National MRLs in Australia were reported. The Table below shows these and the national MRLs previously listed in the 1995 evaluation.

Country	Commodity	MRL, mg/kg
Australia	Apple	0.3
	Pear	0.3
Belgium	Pome fruits	0.2
	Others	0.01
Brazil	Citrus fruits	0.5
	Apple	0.1
France	Apple	0.2
	Grapes	0.2
Japan	Satsuma mandarin	0.5
	Citrus fruits (except Satsuma mandarin)	1
	Apple	1
	Grapes	2
	Hops	15
Spain	Citrus fruits	0.3
	Pome fruits	0.3
	Grapes	0.3
Switzerland	Apples	0.2
	Grapes	0.2

APPRAISAL

Fenpyroximate was first evaluated for toxicity and residues by the 1995 JMPR, which allocated an ADI of 0-0.01 mg/kg bw. That Meeting estimated a maximum residue level of 0.2 mg/kg for apples but this could not be recommended for use as an MRL owing to the lack of critical supporting data.

The Meeting received information on analytical methods with supplementary residue data on oranges, grapes and hops, animal metabolism studies on goats and rats, and an animal feeding study on cows.

Animal metabolism

The metabolism of fenpyroximate in goats was rapid. Small traces of fenpyroximate were found in fat, kidney, muscle and milk. Ten metabolites were identified or characterized. The main compounds found were G-4 *(*(E)-α-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethylene-amino-oxy)-*p*-toluic acid*)* and G-7 *((E)*-α-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy*)-p*-toluic acid*)* in the liver and kidneys, fenpyroximate, G-2 (1-hydroxylmethyl-1-methylethyl *(E)*-α-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy*)-p*-toluate) and G-4 in muscle and fat, fenpyroximate, G-2 and G-9 (4-cyano-1-methyl-5-phenoxy pyrazole-3-carboxylic acid) in milk and M-8 (1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid) and G-9 in urine. The faeces contained fenpyroximate and G-2.

Analytical methods

Analytical methods for fenpyroximate and its isomer were described in the 1995 evaluation. They were based on extraction with methanol and acetone, partitioning with hexane and acetonitrile and clean-up with some combination of C-18 cartridges, gel permeation, silica gel and alumina columns. Determination was by GLC and HPLC. The limits of determination were 0.01 mg/kg for green peppers by HPLC, and 0.1 and 0.2 mg/kg for fruit and tea by GLC.

In the analytical method used for the supervised field trials homogenized orange pulp, orange peel and grapes are extracted with acetone/water twice and centrifuged to separate the phases. The supernatants are collected and adjusted to a volume with acetone/water. An aliquot of the extract is partitioned with dichloromethane (oranges) and ethyl acetate (grapes) after addition of sodium chloride. The organic layer is collected and evaporated. The residue is dissolved in diethyl ether/hexane (1:19) and cleaned up on a silica solid phase extraction (SPE) cartridge, eluted with acetone/hexane (1:1). The eluate is reconstituted in acetonitrile/water (7:3) for quantification by LC-MS. The limits of determination in orange pulp, orange peel and grapes are 0.01, 0.05 and 0.01 mg/kg.

Dried hops are homogenized and extracted with ethyl acetate twice after the addition of water and centrifuged to separate the phases. The organic phases are collected and evaporated. The residue is dissolved in methanol. An aliquot of the extract is partitioned twice with 2,2,4-trimethylpentane after the addition of water and saturated sodium carbonate solution. The organic layer is collected and evaporated. The residue is dissolved in acetonitrile/water (3:10) and cleaned up on a C-18 SPE cartridge, eluted with acetonitrile. The eluate is reconstituted in acetone/water (7:3) for quantification by LC-MS. The limit of determination is 0.01 mg/kg.

In the analytical method used for the processing study on apples homogenized samples of apples, apple juice or apple pomace are extracted by blending with aqueous ethyl acetate and celite. After filtration the extract is evaporated nearly to dryness. The sample is dissolved in ethyl acetate/cyclohexane mixture and cleaned up by GPC. The GPC eluate is further cleaned up on an SPE cartridge eluted with toluene/acetone(95:5). The eluate is concentrated and analysed by gas chromatography with a mass selective detector. The limits of determination are approximately 0.05 mg/kg.

In the analytical methods for animal products used in the animal processing study milk and muscle samples are extracted with acetone and then acetone/water (2:1). The combined extracts are acidified and concentrated to remove acetone, the aqueous solution is extracted with ethyl acetate and the extract partitioned with aqueous sodium carbonate. The ethyl acetate fraction contains fenpyroximate and G-2, while the aqueous fraction contains G-4 and G-9. The ethyl acetate fraction is concentrated and the residue extracted with acetonitrile. The acetonitrile extract is reconstituted in hexane/diethyl ether (9:1) and cleaned up on a silica SPE cartridge, eluted with diethyl ether. Fenpyroximate and G-2 in the eluate are hydrolysed to the common product G-4 which is subsequently methylated with diazomethane. The reaction solution is evaporated and the residue dissolved in hexane/diethyl ether (9:1) and cleaned up on a silica SPE cartridge, eluted with diethyl ether. The eluate is reconstituted in acetone for analysis by GLC with an NPD. The aqueous fraction containing G-4 and G-9 is acidified and extracted with ethyl acetate. The ethyl acetate extract is methylated with diazomethane. The reaction solution is reconstituted in hexane/diethyl ether (9:1) and cleaned up on a silica SPE cartridge eluted with diethyl ether. The eluate is reconstituted in acetone for GLC analysis.

Fat samples are extracted twice with acetonitrile. The combined extracts are concentrated and dissolved in hexane. The hexane solution is partitioned with aqueous sodium carbonate and ammonium hydroxide. The hexane fraction contains fenpyroximate and G-2, while the aqueous fraction contains G-4. The hexane and aqueous fractions are cleaned up and analysed as described for milk and muscle.

Liver and kidney samples are homogenized twice with acetonitrile/water (4:1). The combined supernatant fractions are made up to a volume. An aliquot is partitioned with acetic acid and the aqueous fraction is extracted with acetonitrile. The acetonitrile fraction contains fenpyroxi- mate,G-3 ((E)-2-[4-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneaminooxymethyl)benzoyloxy]-2-methylpropionic acid), G-4 and G-7. The acetonitrile fractions are reconstituted in ethyl acetate. The ethyl acetate solution is cleaned up by GPC and the eluate is methylated with diazomethane and reconstituted in acetonitrile for LC-MS-MS analysis. The limits of determination in the milk and tissues are 0.005 and 0.01 mg/kg.

Stability of residues in stored analytical samples

Animal commodities. Samples were fortified separately with fenpyroximate and various metabolites at 0.1 mg/kg.

Milk was stored frozen for 73-79 days. Recoveries of fenpyroximate, G-2 and G-9 were 89, 83 and 65%. Recoveries of fenpyroximate, G-2 and G-4 were 60, 68 and 47% from muscles stored for 51-56 days, and 67, 37 and 54% from fat stored for 49-54 days. Liver and kidney samples were stored frozen for 53 and 55 days. Recoveries of fenpyroximate, G-7, G-4 and G-3 were 105, 99, 121 and 107% from liver and 86, 88, 81 and 89% from kidneys.

Plant commodities. The storage stability of fenpyroximate in plant commodities was reported in the 1995 monograph. After about 3 years approximately 65% of the initial residue remained on apples and grapes stored at -20°C. In citrus samples fortified with fenpyroximate 65% remained in the pulp stored for 140 days and 72% in peel stored for 188 days. About 100% of the fenpyroximate remained in hops stored at -18°C for 2 years, about 100% of the residues remaining. No new studies were reported.

Definition of the residue

The current residue definition is "fenpyroximate". In new animal metabolism and feeding studies the metabolite G-4 was found in the liver and kidneys and G-2 was found in muscle, fat and milk. However, since toxicity studies on fenpyroximate would include these metabolites they indicate that the metabolites would have little or no potential for toxicity.

The Meeting concluded that the current residue definition is suitable both for compliance with MRLs and for the estimation of dietary intake.

The octanol-water partition coefficient and the results of the animal feeding studies indicate that fenpyroximate is fat-soluble.

Use pattern

Fenpyroximate is an acaricide. National registrations specify only one application per season to avoid the development of resistance.

For tree crops, spray concentration (kg ai/hl) rather than application rate (kg ai/ha) is the prime determinant of GAP for the use of fenpyroximate.

Results from supervised trials

Oranges. Fenpyroximate may be used at 0.005 kg ai/hl (0.1 kg ai/ha) on oranges in Italy with a PHI of 30 days. The residues in whole oranges in four trials in Italy under these conditions were all 0.04 mg/kg and in one trial in Greece in accordance with Italian GAP the residue was 0.07 mg/kg. The residues in the pulp in all five trials were <0.01 mg/kg.

Fenpyroximate may be used at 0.005-0.0075 kg ai/hl on oranges in Spain with a PHI of 14 days. The residues in whole oranges from four trials in Spain and one in Greece under these conditions were 0.04 (2), 0.05 (2) and 0.09 mg/kg. The residues in the pulp were all <0.01 mg/kg.

In Japan, fenpyroximate may be used on mandarins at 0.003-0.005 kg ai/hl with a PHI of 14 days. The residues in mandarins in two trials 14 or more days after treatment according to GAP were 0.04 and 0.21 mg/kg (1995 JMPR).

The residues in oranges from Italy, Spain and Greece were within the same population.

The residues in the whole oranges from 4 Italian trials, 4 Spanish trials and 1 Greek trial according to GAP in rank order were 0.04 (6), 0.05 (2) and 0.09 mg/kg. All the 9 residues in the pulp were <0.01 mg/kg.

The Meeting estimated a maximum residue level and an STMR level for fenpyroximate in oranges of 0.2 mg/kg and 0.01 mg/kg respectively.

Apples. Fenpyroximate may be used at 0.008 kg ai/hl (0.06-0.08 kg ai/ha) on apples in France with a PHI of 21 days. The residues in apples from five French trials, ten German trials and one Belgian trial in accordance with French GAP were 0.03, 0.09, 0.06, 0.11, 0.16, 0.1, 0.09 (2), 0.12, 0.16, 0.12, 0.06, 0.15, 0.08 and <0.05 mg/kg.

Fenpyroximate may be used at 0.005 kg ai/hl (0.075-0.175 kg ai/ha) on apples in Australia with a PHI of 14 days. The residues in apples from four Australian trials were 0.18, 0.14, 0.12 and 0.17 mg/kg and from seven trials in New Zealand in accordance with Australian GAP were 0.05, 0.04, 0.03, 0.08 and 0.06 (3) mg/kg.

Fenpyroximate may be used at 0.0025 kg ai/hl (0.05-0.075 kg ai/ha) on apples in New Zealand with a PHI of 28 days. The residues in apples from seven trials in New Zealand meeting these conditions were <0.01 (2), 0.01, 0.03 and 0.02 (3) mg/kg.

The residues from France and Australia, and those from New Zealand complying with Australian GAP, were in a single population, but those from trials according to New Zealand GAP cannot be combined with the others since the PHI is longer and the spray concentration is lower.

The fenpyroximate residues in trials according to French and Australian GAP in rank order (median underlined) were <0.05, 0.03 (2), 0.04, 0.05, 0.06 (5), 0.08 (3), 0.09 (3), 0.1, 0.11, 0.12 (3), 0.14, 0.15, 0.16 (2), 0.17 and 0.18 mg/kg

The Meeting estimated a maximum residue level of 0.3 mg/kg and an STMR of 0.09 mg/kg for fenpyroximate in apples.

Grapes. Fenpyroximate may be used at 0.005 kg ai/hl (0.05 kg ai/ha) on grapes in Italy with a PHI of 28 days. The residues in the grapes from four trials in Italy meeting these conditions were 0.02, 0.03 and 0.04 (2) mg/kg. Fenpyroximate is not registered in France but one trial at the spray concentration of 0.006 kg ai/hl was considered to be in accordance with Italian GAP. The residue was <0.02 mg/kg.

Fenpyroximate may be used at 0.0075-0.01 kg ai/hl (0.1 kg ai/ha) on grapes in Spain with a PHI of 14 days. The residues in grapes from four trials in Spain meeting these conditions were 0.06 and 0.04 (3) mg/kg. Two trials in France at 0.006 and 0.008 kg ai/hl and five trials in Italy at 0.0062-0.013 kg ai/hl were considered to be in accordance with Spanish GAP. The residues were <0.02, 0.07, 0.08, 0.17, 0.19, 0.47 and 0.57 mg/kg.

In Japan, fenpyroximate may be used at 0.003-0.005 kg ai/hl on grapes with a PHI of 14 days. The residues in grapes from four trials meeting these conditions were 0.41, 0.45, 0.53 and 0.51 mg/kg.

The residues from the trials in Spain, France, Italy and Japan were in the same population.

The fenpyroximate residues in the combined Spanish, French, Italian and Japanese trials according to GAP in rank order (median underlined) were <0.02, 0.02, 0.03, 0.04(5), 0.06, 0.07, 0.08, 0.17, 0.19, 0.41, 0.45, 0.47, 0.51, 0.53 and 0.57 mg/kg.

The Meeting estimated a maximum residue level and an STMR level for fenpyroximate in grapes of 1 mg/kg and 0.07 mg/kg respectively.

Hops. Fenpyroximate may be used at 0.0075 kg ai/hl (0.225-0.263 kg ai/ha) on hops in Germany with a PHI of 21 days. The residues in hops from twelve trials in Germany meeting these conditions in rank order were <1, 1.2, 2.1(2), 3.7, 4.3, 4.4, 5.0, 5.9, 6.2, 7.4 and 8.4 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 4.4 mg/kg for fenpyroximate on hops.

Processing

Apples. In four processing studies the mean processing factor from fresh apples to apple juice was 0.42 and that from apples to wet pomace was 5.1. The 1995 JMPR evaluated a processing study in which the residues in the fruit were 0.06 and 0.15 mg/kg and those in apple purée were <0.05 (2) mg/kg, giving processing factors for apple purée of <0.83 and <0.24 (mean <0.54). Since the estimated STMR for apples is 0.09 mg/kg, the calculated STMRs for apple juice and purée are 0.09 × 0.42 = 0.038 and 0.09 × 0.54 = 0.049.

The Meeting estimated STMRs for apple juice of 0.04 mg/kg and for apple purée of 0.05 mg/kg.

Grapes. The processing study reported in the 1995 JMPR monograph showed residues in wine of <0.01 mg/kg from residues in fresh grapes of 0.15, 0.13 and 0.14 mg/kg, giving processing factors for wine of

<0.07, <0.08 and <0.07 (mean <0.07). The STMR for grapes is 0.07 mg/kg, so the calculated STMR for wine is 0.07 × 0.07 = 0.0049 mg/kg.

Hops. In the processing study reported in 1995, beer containing residues of <0.01 mg/kg was brewed from dried hops containing residues of 6.4, 9.0, 11.4 and 37.4 mg/kg giving processing factors for beer of <0.0016, <0.0011, <0.0009 and <0.0003 (mean <0.001).

The Meeting estimated an STMR for beer of 0.0044 mg/kg from the STMR for hops of 4.4 mg/kg.

Animal feeding studies

Dairy cattle dosed at a level equivalent to 1, 3 or 10 ppm in the feed showed mean total residues of fenpyroximate and its metabolite G-2 of <0.01, 0.015 and 0.038 mg/kg in muscle, 0.015, 0.056 and 0.11 mg/kg in fat, <0.003, <0.003 and <0.01 mg/kg in liver, and <0.003, <0.01 and 0.014 mg/kg in kidney. The residues in the milk of the high-dose group were 0.007 to 0.017 mg/kg.

The concentration factors for wet apple pomace from processing studies were 4.0 to 6.0 (mean 5.1).

Assuming a dry matter content of 40% in wet apple pomace and maximum incorporation rates of dry apple pomace of 20 and 40% in dairy and beef cattle diets respectively, the maximum feed intakes will be approximately 0.25 and 0.5 ppm.

0.09 mg/kg × 5.1/40% × 20% (40%) = 0.25 ppm (0.5 ppm)

The residues were below the LOD in muscle at the 1 ppm feeding level, in kidneys at 1 and 3 ppm, and in liver at 1, 3 and 10 ppm. Residues were detected in the fat and milk at the 1, 3 and 10 ppm feeding levels. The Meeting noted that the calculated dietary burdens of 0.5 ppm for beef cattle and 0.25 ppm for dairy cattle were close the lowest feeding level of 1 ppm.

In the animal feeding study, the lowest feeding level showed <0.01 mg/kg in muscle, 0.018 mg/kg in fat and <0.003 mg/kg in kidney and liver. Milk from the low-dose group was not analysed. The calculated maximum dietary burden was 1/6th of the 3 ppm feeding level, in which the highest milk residue was 0.011 mg/kg. The calculated milk residue from the estimated dietary burden is therefore 0.002 mg/kg. Liver and kidney may contain residues of the polar metabolite G-4 at an estimated maximum of 0.1 mg/kg from the calculated dietary level.

The Meeting estimated maximum residue levels of 0.02 mg/kg for cattle meat (fat), 0.01* mg/kg for cattle kidney and liver and 0.005* mg/kg for cattle milk, and STMRs of 0.01 mg/kg for cattle meat, 0 mg/kg for cattle liver and kidney, and 0.002 mg/kg for cattle milk.

RECOMMENDATIONS

On the basis of the available data on residues resulting from supervised trials the Meeting estimated the maximum residue and STMR levels listed below. The maximum residue levels are recommended for use as MRLs.

Definition of residue for compliance with the MRL and for estimation of dietary intake: fenpyroximate.

The residue is fat-soluble

Commodity		MRL, mg/kg	STMR, mg/kg	HR/HR-P, mg/kg[1]
CCN	Name			

Commodity		MRL, mg/kg	STMR, mg/kg	HR/HR-P, mg/kg[1]
CCN	Name			
FP 0226	Apple	0.3	0.09	0.18
JF 0226	Apple juice		0.04	<0.05
	Apple purée		0.05	<0.05
	Beer		0.005	<0.01
MO 1280	Cattle kidney	0.01*	0	
MO 1281	Cattle liver	0.01*	0	
MM 0812	Cattle meat	0.02(fat)	0.01	
ML 0812	Cattle milk	0.005* F	0.002	
FB 0269	Grapes	1	0.07	0.57
DH 1100	Hops	10	4.4	8.4
FC 0004	Oranges, Sweet, Sour	0.2	0.01	0.09
	Wine		0.004	<0.01

[1] HR: highest residue (edible portion) from supervised trials. HR-P: highest residue processed commodity, calculated from the HR of the raw agricultural commodity and the processing factor.

FURTHER WORK OR INFORMATION

Desirable

An additional study of processing grapes to wine and raisins.

The Meeting was informed that the results of a study of processing grapes to raisins, pomace, forage and juice would be available in the year 2000.

DIETARY RISK ASSESSMENT

Chronic intake

STMRs have been estimated for 9 commodities. The International Estimated Daily Intakes for the five GEMS/Food regional diets were in the range of 0-1% of the ADI. The Meeting concluded that the intake of residues of fenpyroximate resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The international estimated short-term intake (IESTI) for fenpyroximate was calculated as described in Section 3 for the commodities for which maximum residue levels and STMRs were estimated and for which consumption data (large portion consumption, unit weight) were available. The results are shown in Annex IV. The IESTI varied from 0 to 0.008 mg/kg bw in the general population and from 0 to 0.032 mg/kg bw in children. As no acute reference dose has been established, the risk assessment for fenpyroximate was not finalized.

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FOLPET (41)

EXPLANATION

Folpet was first evaluated in 1969 and has been reviewed several times since, most recently in 1998 for residues in the CCPR Periodic Review Programme. The 1998 JMPR did not receive information on the environmental fate of folpet in soil or in water/sediment systems and (1) agreed that its estimates of maximum residue levels should not be recommended for use as MRLs until these critical supporting studies could be evaluated, and (2) recommended withdrawal of existing CXLs and draft MRLs. The 1998 JMPR was informed at a late stage that studies were available on aerobic and anaerobic degradation and photolysis in soil, field dissipation, adsorption and desorption, soil mobility, leaching of aged residues and aqueous photolysis. Details of the studies were provided to the present Meeting.

Updated information on GAP and new labels have also been provided.

METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

The Meeting received information on the metabolism of folpet in potatoes to supplement previously evaluated metabolism studies on tomatoes, winter wheat, grapes and avocados.

Crowe *et al.* (1999) applied [U-*phenyl*-^{14}C]folpet 5 times to potato plants (Maris Piper variety) in pots at the equivalent of 1.86-1.95 kg/ha at 77, 57, 37, 17 and 7 days before harvest. Plant samples were taken 2-4 hours after the first, third and fifth treatments, 3 days before harvest and at harvest.

The potato foliage was washed with acidified acetonitrile, and subsequently homogenized and extracted. Tubers were treated similarly, but the washings were considered to include residues in the soil rather than on the tubers. Levels of ^{14}C expressed as folpet were in the range 57-110 mg/kg in the foliage (washings + homogenates) and 0.56-1.1 mg/kg in the tuber homogenates, except in the samples taken after the first treatment in which no residue was detected.

Almost all (90-98%) of the ^{14}C associated with the foliage was washed off the surface by the acetonitrile, and the residues in the washings were almost exclusively folpet. Most of the remaining ^{14}C in the foliage was extractable. In the tubers, 86-93% of the ^{14}C was extractable with acetonitrile, and phthalic and phthalamic acids accounted for most of the residue (Table 1); folpet itself constituted only about 0.1%. Conjugated and bound metabolites (about 10% at harvest) were released by hydrolysis and EDTA treatment. Natural incorporation into proteins and sugars accounted for 1.3% of the ^{14}C in the tubers at harvest.

The Meeting concluded that the metabolism of folpet in potatoes was similar to that in other plants and that folpet itself was not translocated to the tubers.

Table 1. Compounds identified in tubers from potato plants treated with 5 applications of [U-*phenyl*-^{14}C]folpet at 1.86-1.95 kg ai/ha (Crowe *et al.*, 1999).

Compound or fraction	^{14}C expressed as folpet, mg/kg			
	37 days before harvest	7 days before harvest	3 days before harvest	At harvest
Folpet	-	0.001	0.001	0.001
Phthalimide	-	0.005	0.003	0.005
Phthalamic acid	0.14	0.28	0.20	0.27
Phthalic acid	0.28	0.37	0.33	0.60
Acid conjugates	-	0.059	-	0.038
Total ^{14}C (by combustion)	0.56	0.86	0.71	1.1

Environmental fate in soil

The Meeting received information on aerobic and anaerobic degradation, leaching characteristics of the aged residue, adsorption and desorption, field dissipation and microbiological mineralization.

Daly (1991a) incubated [U-*phenyl*-^{14}C]folpet at 11.9 µg/g in a microbiologically active sandy loam soil (pH 5.4, 2.0% organic matter, 17% clay) under aerobic conditions at 25°C in the dark for 12 months. The soil moisture level was maintained at 75-80% of field capacity. The recovery of the ^{14}C was 92.5%. Unextractable ^{14}C peaked at 9.2% of the dose on day 15 and decreased to 5.0% after 12 months. A preliminary 14-day study had shown that the half-life of folpet was 8 days.

The fate of folpet during the 12-months aerobic incubation is indicated in Table 2. The depletion of folpet was biphasic, with an estimated half-life of 4.3 days during the first 14 days, but a half-life of 167 days calculated during 14-365 days. Phthalimide, the main degradation product apart from CO_2, accumulated for the first few days, accounting for 65% of the dose on day 5, and then decreased to similar levels to those of folpet after 14 days. Phthalic acid was a minor product, constituting less than 6% of the applied dose and 20-30% of the identified residue after about 2 months. Half of the folpet was converted to CO_2 in the first month, demonstrating mineralization of the benzene ring, but the subsequent rate of formation was much slower.

Table 2. Degradation of folpet during aerobic incubation of [U-*phenyl*-^{14}C]folpet with soil for one year (Daly, 1991a).

Days	^{14}C, % of dose, as			
	Folpet	Phthalimide	Phthalic acid	Evolved CO_2
0	87	7.7	3.6	0
1	79.6	17.6	2.6	0
2	67.5	31.1	3.1	0
3	35.5	49.4	3	0.3
4	22.3	57.2	3.7	0.5
5	20.9	64.9	5.7	2.4
7	16.2	58.3	2.4	5.7
14	10.1	10.1	1.4	36
31	6.8	6.2	2.4	49
61	4.9	4.1	2.6	56
92	4.1	3.6	2.2	60
122	3.4	2.4	2	63
184	2.9	2.1	1.8	65
273	2.1	1.6	1.4	68
365	2	1.3	1.4	70

Pack (1976) incubated [*carbonyl*-^{14}C]folpet at 6 µg/g in a sandy loam soil (pH 6.8, 1.8% organic matter, 16% clay) under aerobic conditions at laboratory temperatures for 1 year. About 50%, 90% and 98% of the dose was liberated as $^{14}CO_2$ after 6, 25 and 365 days. Less than 10% of the applied folpet remained intact after 7 days.

Levels of the radioactive compounds identified and assayed by TLC are shown in Table 3. The three identified products reached their highest levels, less than 2% of the applied ^{14}C, by day 7 and then decreased. The unextractable residues amounted to no more than a few per cent of the dose at any time. *N*-hydroxyphthalimide, 3-hydroxyphthalimide and 4-hydroxyphthalimide were sought but not detected (<0.01 mg/kg).

Table 3. Degradation of folpet during the incubation of [*carbonyl*-^{14}C]folpet with a sandy loam soil under aerobic conditions (Pack, 1976).

Days	^{14}C, % of dose, as			
	Folpet	Phthalimide	Phthalic acid	Phthalamic acid
0	97	1.40		
7	9.9	1.98	1.76	1.09
14	1.6	0.32	0.08	0.11
34	1.35	0.52	0.13	0.16
59	0.40	0.15		0.05
118	0.41	0.18		
181	0.30	0.13		
240	0.32	0.10		
365	0.28	0.06		

Daly (1991b) incubated [U-*phenyl*-^{14}C]folpet at 9.8 µg/g in a microbiologically active sandy loam soil (pH 5.4, 2.0% organic matter, 17% clay) under aerobic conditions at 25°C in the dark for 4 days, after which the soil was flooded and the system purged with nitrogen to remove oxygen and incubation was then continued anaerobically for 60 days. The recovery of the ^{14}C was 98.9%. The results are shown in Table 4. Unextractable residues did not exceed 3.3% of the dose. A high proportion of the phthalimide and phthalic acid was present in the water rather than on the soil.

After the aerobic incubation phthalimide was the main component of the residue and remained so throughout the anaerobic phase. The estimated half-life of folpet during the anaerobic phase was 15 days. The rate of mineralization was slower than in the aerobic incubation. Phthalimide and phthalic acid were quite persistent under anaerobic conditions. Phthalamic acid was not detected.

Table 4. Degradation of folpet during anaerobic incubation of [U-*phenyl*-^{14}C]folpet with soil for 60 days, after preliminary aerobic ageing for 4 days (Daly, 1991b).

Days	^{14}C, % of dose, as			
	Folpet	Phthalimide	Phthalic acid	Evolved CO_2
AEROBIC				
0	88.0	8.7	0	0
1	77.2	19.1	0	0
2	63.8	27.7	3.8	0.11
3	41.6	41.7	5.4	1.8
4	28.1	46.4	4.9	6.1
ANAEROBIC				
0	27.6	50.6	5.0	6.2
3	20.4	47.5	6.4	6.5
15	11.0	50.2	3.8	14.4
30	7.6	46.4	9.2	21.6
45	5.1	46.0	5.6	25.1
60	3.6	36.3	13.3	26.4

Pack (1980) incubated [*carbonyl*-^{14}C]folpet at 5 µg/g in a loamy sand soil (pH 7.3, 1.4% organic matter, 9.3% clay) under anaerobic conditions at 25°C for 1 year. About 50% and 79% of the dose was liberated as $^{14}CO_2$ after 119 and 365 days respectively. After 371 days approximately 20% of the dose remained in the soil. Folpet itself had completely disappeared by the first sampling after 7 days. Phthalic acid was the main product and was quite persistent, but decreased from 45 to 19% of the AR in 8 months. The composition of the identified residue is shown in Table 5.

Table 5. Composition of the identified residue in a loamy sand soil during the anaerobic incubation of [*carbonyl*-^{14}C]folpet at 5µg/g (Pack, 1980).

Days	^{14}C, % of dose, as			
	folpet	phthalimide	phthalic acid + phthalamic acid	2-cyanobenzoic acid
7	<0.1	1.2	36	7.5
112	<0.1	0.7	45	0.5
187	<0.1	0.2	42.8[1]	5.7
365	<0.1		19	0.1

[1] phthalic acid 42.3%, phthalamic acid 0.5%

Rhoads (1991a) applied [U-*phenyl*-^{14}C]folpet to 1 mm layers of sterilized (autoclaved) sandy loam soil on TLC plates and exposed the plates to natural sunlight and artificial light. The photolytic half-lives of folpet were 17 days in sunlight and 68 days in artificial light, while the half-lives in the corresponding dark controls were 7.3 and 43 days respectively. Longer half-lives of folpet under irradiated than under dark conditions are difficult to interpret, but rapid chemical hydrolysis of folpet in some situations may render photolysis relatively unimportant.

In field dissipation studies in Florida (Polk County and Seminole County) Creeger (1991a,b) applied a folpet WP to citrus groves three times at 2-week intervals at a rate of 6.7 kg ai/ha per application and determined folpet and phthalimide at intervals in soil samples. The Polk soil was a sand, pH 5.8, with 0.9% organic matter in the surface soil and the Seminole soil was a pH 4.6 sand with 1.9% organic matter at the surface. The results are shown in Table 6. Folpet and phthalimide were detected mainly in the surface layers and had disappeared within one week of the final treatment. The rapid disappearance agrees with the results of laboratory studies.

Table 6. Folpet and phthalimide in soil profiles at intervals after citrus groves had been treated with folpet (Creeger, 1991a,b).

Days	Residues, mg/kg, at depths of									
	0-15 cm		15-30 cm		30-45 cm		45-60 cm		60-90 cm	
	Folpet	Phthalimide	Folpet	Phthalimide	Folpet	Phthalimide	Folpet	Phthalimide	Folpet	Phthalimide
POLK COUNTY										
Application 1										
0	0.09	0.04	0.10	ndr	0.06	ndr	ndr	ndr	ndr	ndr
Application 2										
0	0.09	0.09	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
Application 3										
0	0.30	0.07	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
1	0.80	0.06	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
3	0.12	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
7	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
14	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
21	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
28	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
60	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr

Days	Residues, mg/kg, at depths of									
	0-15 cm		15-30 cm		30-45 cm		45-60 cm		60-90 cm	
	Folpet	Phthalimide	Folpet	Phthalimide	Folpet	Phthalimide	Folpet	Phthalimide	Folpet	Phthalimide
120	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
SEMINOLE COUNTY										
Application 1										
0	0.25	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
Application 2										
0	0.30	0.05	0.25	ndr	0.05	ndr	ndr	ndr	ndr	ndr
Application 3										
0	0.16	ndr	0.23	0.05	0.10	ndr	ndr	ndr	ndr	ndr
1	0.13	ndr	0.07	ndr	0.20	ndr	ndr	ndr	ndr	ndr
3	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
7	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
14	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
21	ndr	ndr	0.05	ndr	ndr	ndr	ndr	ndr	ndr	ndr
28	ndr	ndr	0.12	ndr	ndr	ndr	ndr	ndr	ndr	ndr
60	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr
120	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr	ndr

ndr: no detected residues (<0.05 mg/kg)

Ver Hey (1988) measured the adsorption and desorption of [U-*phenyl*-^{14}C]folpet on four soils. Soil (1 g) was mixed with 5 ml of a solution of folpet (0.04, 0.1, 0.2 or 1 µg/ml) in 0.01 M calcium chloride and shaken for 24 hours at 25°C in the dark. ^{14}C levels were measured in the clear aqueous layer separated by centrifuging. To measure desorption the residual soil was mixed with 5 ml of 0.01 M calcium chloride and shaken for 24 hours at 25°C in the dark, and ^{14}C levels were again determined in the aqueous phase. The organic carbon content of the soil was taken as 1/1.7 x (% organic matter) in calculating K_{oc}. $K_{oc} = 100 \times K_d/(\%$ organic carbon). The soil characteristics and adsorption and desorption constants are shown in Table 7. Folpet was strongly adsorbed to the soils and was not readily desorbed.

It is quite likely that much of the folpet had been hydrolysed to phthalimide and phthalic acid during the 24 hours in solution, so the calculated K_d and K_{oc} do not necessarily apply to folpet itself but to the mixture of folpet and its hydrolysis products.

Table 7. Soil characteristics and adsorption-desorption properties for [U-*phenyl*-^{14}C]folpet on four soils (Ver Hey, 1988).

Soil	% organic matter	CEC meq/100 g	pH	% sand	% silt	% clay	adsorption		desorption	
							K_d	K_{oc}	K_d	K_{oc}
Loamy sand	3.0%	2.6	5.1	86%	10%	4%	0.22	12	0.11	6.3
Sandy loam	2.9%	2.9	5.3	68%	18%	14%	0.13	7.4	0.042	2.5
Loam	1.3%	8.7	6.9	52%	29%	19%	0.17	22	0.042	5.5
Silt loam	1.4%	11.2	8.0	16%	65%	19%	0.17	21	0.066	8.0

Pack (1977) rated folpet as very slightly mobile after TLC on 5 soils (a silty clay loam, a clay loam, an adobe clay, a sandy loam and a clay loam). From the data he calculated the corresponding K_d values, which ranged from 6 to 67 (Pack, 1987). However, the measured R_f values were small and the report did not state whether the system was checked for overloading with folpet. If the amount of folpet exceeded its solubility in the aqueous phase much would remain at the origin, and the relationship between the measured R_f and K_d:

$$K_d = \frac{\frac{1}{R_f} - 1}{d_s - 1}$$

when d_s is the density of the soil (= 2.5) would be invalid.

Rhoads (1991b) examined the leaching of aged residues of [U-*phenyl*-^{14}C]folpet (30 days aerobic incubation of 10 mg/kg at 25°C) in a sandy loam (68% sand, 18% silt, 14% clay, 2.9% organic matter, pH 5.3). At the end of the 30 days about 40% of the ^{14}C had been lost as CO_2. After the aerobic incubation, 10 g portions of treated soil were applied to untreated soil columns and followed by an overlay of untreated soil. During 45 days leaching the columns of soil were treated 3 times a week with 0.02 N calcium chloride solution equivalent to 12.5 mm rain and twice a week with 25 mm. At the end of the 45 days the columns were sectioned in 25 mm lengths and assayed for ^{14}C.

Less than 0.06% of the applied ^{14}C was found in the leachate in the first 10 days of leaching and essentially none thereafter. Most of the residue remained in the top soil segment (Table 8), showing low mobility of folpet and its degradation products in this soil.

Table 8. Vertical distribution of ^{14}C in soil columns after 45 days leaching of aerobically aged [U-*phenyl*-^{14}C]folpet (Rhoads, 1991b).

	Soil segment, mm depth											
	0-25	25-50	50-75	75-100	100-125	125-150	150-175	175-200	200-225	225-250	250-275	275-300
^{14}C, % of applied	64	11	1.5	0.20	0.20	0.36	0.12	0.06	0.49	0.08	0.07	0.12

Jenkins (1994) showed that 27.5 mg technical folpet/l (10 mg carbon/l) did not significantly inhibit bacterial degradation of the reference material sodium benzoate in a 5-day test and therefore folpet could be tested for bacterial degradation in a modified Sturm Test. However, the pH of the test mixtures was in the range 7.2-7.7, so folpet would be converted abiotically in hours to phthalimide and further to phthalic acid, and so would not be present to exert any biological effect. The report suggests that folpet was not significantly degraded under the conditions of the test, but the suggestion is based on lack of oxygen consumption by the biological system and has not taken into account possible abiotic hydrolysis.

The production of CO_2 from technical folpet and sodium benzoate by the bacterial inoculum at the same carbon concentration was compared in parallel tests for 29 days. The degradation of folpet was slow but progressive, with about 12% of theoretically available carbon released as CO_2 after 7 days and 41% after 29 days; folpet may be classed as inherently degradable. Sodium benzoate, classed as readily degradable, released 70% and 97% of its carbon as CO_2 after 7 and 29 days respectively.

Jenkins *et al.* (1998) tested the biodegradability of [U-*phenyl*-^{14}C]folpet in a modified Sturm Test. The ring carbons were labelled as they were the most stable part of the molecule and production of $^{14}CO_2$ would indicate mineralization of the folpet. The reaction medium was three litres of aqueous mineral salts solution inoculated with activated sewage sludge and containing 3 mg folpet. The pH of the test and control mixtures was 7.5-7.8. The evolved $^{14}CO_2$ was monitored for 28 days with the reaction mixture held at 20-24°C.

At the pH of the test mixture folpet would have been converted abiotically to phthalimide and further to phthalic acid within hours. The test should then parallel a test on phthalic acid.

Degradation was quite rapid from 4 to 14 days, with the evolved $^{14}CO_2$ increasing from about 10% to 60% of the dose, with slower degradation after 19 days. Some 16-18% of the ^{14}C had been incorporated into sewage solids by day 28.

Table 9. Degradation of [U-*phenyl*-^{14}C]folpet and the reference sodium benzoate in a modified Sturm test (Jenkins *et al.*, 1998).

Incubation time, days	Sodium benzoate, % degradation	Folpet, cumulative % of applied ^{14}C evolved as $^{14}CO_2$ - duplicate runs	
1	2	0.077	0.12
2	22	0.40	0.53
4	44	11.6	13.7
6	62	30	33
9	75	49	51
12	82	58	60
14	84	62	63
19	86	67	68
22	88	69	71
26	90	71	73
28	91	72	74

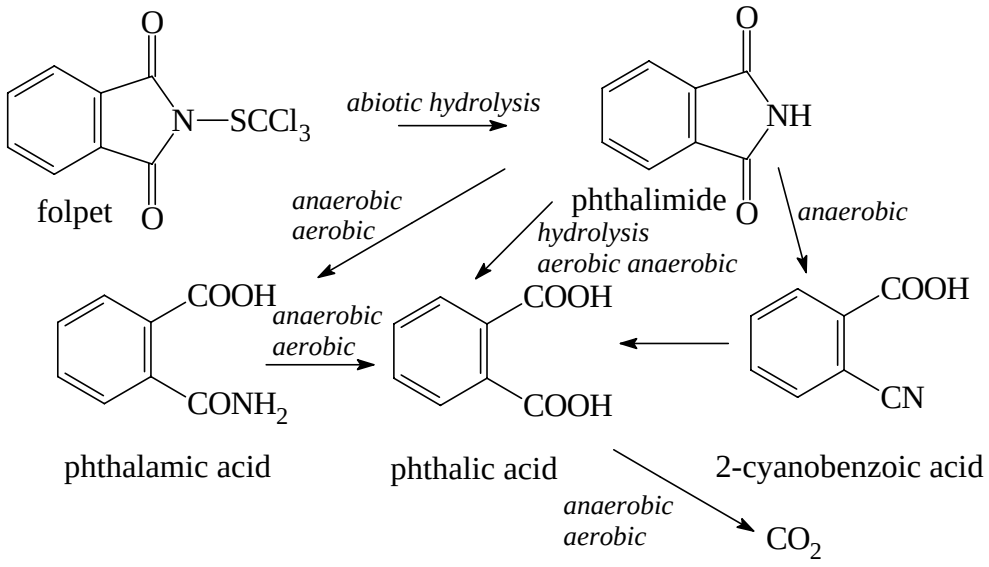

Figure 1. Degradation of folpet in soil.

Environmental fate in water/sediment systems

The Meeting received reports of the aqueous hydrolysis and photolysis of folpet, and a summary report of a recently completed study of the fate of folpet in a water/sediment system.

Ruzo and Ewing (1988) incubated [*carbonyl*-^{14}C]folpet at approximately 1 mg/l in sterile aqueous buffered solutions (ionic strength 0.01) at 25°C in the dark. The folpet was dissolved in

acetonitrile and added to the buffers, 1 ml to 150 ml. The hydrolysis half-lives were 2.6 hours at pH 5, 1.1 hours at pH 7 and 67 seconds at pH 9. The solubility of folpet in water was quoted from previous work as 1.25 mg/l at 25°C. One product was described as 'phthalimic acid', but appeared to be phthalamic acid.

Table 10. Hydrolysis of folpet at pH 5, 7 and 9 (Ruzo and Ewing, 1988).

pH	Time	% of ^{14}C due to			
		folpet	phthalimide	phthalamic acid	phthalic acid
5	24 hours	0.5	91	0.6	8.5
7	8 hours	3.0	44	2.5	46
9	10 minutes	0.25	15	0.7	78

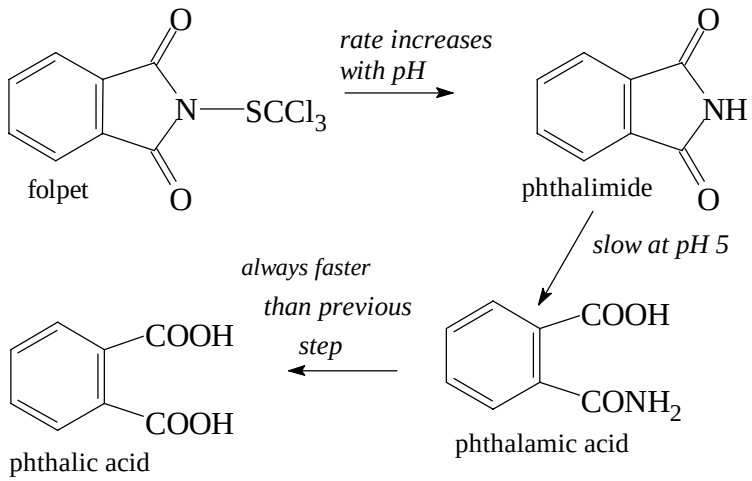

Figure 2. Folpet products of hydrolysis (Ruzo and Ewing, 1988).

Concha and Ruzo (1992) hydrolysed [*trichloromethyl*-^{14}C]folpet at approximately 1 mg/l in sterile aqueous buffered solutions at 25°C in the dark. At pH 5 47% and 15% of the ^{14}C remained as folpet after 1 and 24 hours, and at pH 7 52% after 1 hour and 1.1% after 24 hours. No folpet remained after 1 hour at pH 9. The products of decomposition apart from CO_2 were not definitely identified, but probably included trichloromethanethiol (at pH 7) and COS.

Ruzo (1989) exposed [*carbonyl*-^{14}C]folpet at about 1 mg/l in aqueous pH 3 buffer to natural sunlight and ultraviolet light (maximum intensity at 350 nm) for 8 hours at 25°C. The rates of breakdown and the products were the same for samples kept in the dark and those exposed to UV light, indicating that hydrolysis is a more important mechanism of breakdown than photolysis.

Crowe (1999) provided a brief summary report of a study of the fate of [U-*phenyl*-^{14}C]folpet in two water/sediment systems, one with a silty clay sediment (pH 6.8, 4.4% organic C) and the other with a sandy loam sediment (pH 5.9, 1.2% organic C). The nominal folpet dose was equivalent to 1.6 kg/ha. The systems were incubated in the dark. Folpet was converted to CO_2, phthalimide, phthalamic acid, phthalic acid, polar material and several unidentified compounds. Folpet itself disappeared very quickly.

USE PATTERN

Folpet is a broad spectrum, non-systemic fungicide used on both food and non-food crops. The major uses are against diseases of grapes, pome and stone fruit and vegetables. The Meeting was provided with updated information on registered uses of folpet and labels from many countries. Table 11 summarizes the new information and also includes much of the information on GAP provided to the 1998 JMPR.

Table 11. Registered uses of folpet.

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Apples	Argentina	WP	foliar		0.12		15
Apples	Canada	WP	foliar		0.075-0.10		1
Apples	Chile	WP	foliar	1.5-2.0	0.09-0.11		7
Apples	France	WP	foliar		0.1		
Apples	Hungary	WP	foliar	1.5			10
Apples	Mexico	WP	foliar		0.10-0.13		7
Apples	Portugal	WP	foliar		0.13		21
Apples	Spain	WP	foliar		0.13-0.15		10
Apples	Switzerland	WG	foliar		0.08		21
Avocado	Mexico	WP	foliar		0.10-0.12		30
Celery	Honduras	WP	foliar	0.64			3
Celery	Mexico	WP	foliar	1.0-2.0			7
Citrus fruits	Mexico	WP	foliar		0.10-0.12		7
Cranberries	Canada	WP	foliar	5.0	0.25		30
Cucumbers	Argentina	WP	foliar		0.12		7
Cucumbers	Canada	WP	foliar	1.0-2.0	0.10-0.20		7
Cucumbers	Cyprus	WP	foliar	1.0	0.1		2
Cucumbers	Hungary	WP	foliar		0.10-0.13		14
Cucumbers	Israel	WP	foliar	2.0			7
Cucumbers	Mexico	WP	foliar	1.2-1.7			3
Garlic	Mexico	WP	foliar	1.0-1.4			7
Grapes	Canada	WP	foliar		0.10		1
Grapes	Chile	WP	foliar	1.5-2.0	0.10-0.15		14
Grapes	France	WP	foliar		0.15		
Grapes	France [1]	SC	foliar	1.0-1.5			21, 30
Grapes	France [1]	WG	foliar	1.0-1.5			21, 28
Grapes	France [1]	WP	foliar	1.0-1.8			28
Grapes	Mexico	WP	foliar	1.0-1.2			10
Grapes	Spain	WP	foliar		0.15-0.20		21
Grapes, table	Argentina	WP	foliar		0.10-0.13		7
Grapes, table	Italy	WG	foliar		0.16		10
Grapes, wine	Argentina	WP	foliar		0.10-0.13		20
Grapes, wine	Germany [2]	WP	foliar		0.06	3	35
Grapes, wine	Italy	WG	foliar		0.16		40
Lettuce	Greece	SC	foliar		0.13-0.16		
Lettuce	Hungary	WP	foliar		0.10-0.13		14
Lettuce	Mexico	WP	foliar	1.2			7
Lettuce	Portugal	WP	foliar		0.10-0.13		14
Lettuce	Spain	WP	foliar		0.13-0.15		21
Melons	Argentina	WP	foliar		0.12		7
Melons	Canada	WP	foliar	2.0-4.0	0.10-0.20		1
Melons	Costa Rica	WP	foliar	0.10-0.13	0.10-0.13		7
Melons	El Salvador	WP	foliar	0.10-0.13	0.10-0.13		7
Melons	Greece	SC	foliar		0.13-0.16		20
Melons	Guatemala	WP	foliar	0.38			3
Melons	Honduras	WP	foliar	0.64	0.16		3

Crop	Country	Form	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Melons	Mexico	WP	foliar	1.2-1.7			7
Onions	Argentina	WP	foliar		0.12-0.13		7
Onions	Chile	WP	foliar	1.5-2.0	0.10-0.13		7
Onions	Costa Rica	WP	foliar	0.10-0.13	0.10-0.13		7
Onions	El Salvador	WP	foliar	0.10-0.13	0.10-0.13		7
Onions	Greece	SC	foliar		0.13-0.16		20
Onions	Honduras	WP	foliar	0.64			3
Onions	Hungary	WP	foliar		0.10-0.13		14
Onions	Mexico	WP	foliar	1.2-1.4			7
Onions	Portugal	WP	foliar		0.10-0.13		7
Potato	Argentina	WP	foliar		0.12-0.18		7
Potato	Chile	WP	foliar	1.0-1.7	0.10-0.15		7
Potato	Israel	WP	foliar	2.0			7
Potato	Mexico	WP	foliar	1.7-1.9			30
Potato	Poland	WG	foliar				23
Potato	Spain	WP	foliar		0.13-0.15		10
Potato	Ukraine	WG	foliar	1.5			20
Strawberries	Argentina	WP	foliar		0.13		7
Strawberries	Canada	WP	foliar	2.0	0.10		1
Strawberries	Chile	WP	foliar	1.5-2.0	0.10-0.15		7
Strawberries	Costa Rica	WP	foliar	0.10	0.10		7
Strawberries	El Salvador	WP	foliar	0.10	0.10		7
Strawberries	Honduras	WP	foliar	0.10	0.10		3
Strawberries	Mexico	WP	foliar	0.72-1.2			2
Strawberries	Netherlands	WP	field		0.13		4
Strawberries	Netherlands	WP	glasshouse		0.13		14
Strawberries	Spain	WP	foliar		0.13-0.15		21
Summer squash	Mexico	WP	foliar	1.2-1.7			3
Tomato	Argentina	WP	foliar		0.13-0.14		7
Tomato	Canada	WP	foliar	4.0	0.20		1
Tomato	Chile	WP	foliar	1.0-1.9	0.10-0.15		7
Tomato	Costa Rica	WP	foliar	0.13	0.13		7
Tomato	El Salvador	WP	foliar	0.13	0.13		7
Tomato	Honduras	WP	foliar	0.13	0.13		3
Tomato	Hungary	WP	foliar		0.10-0.13		14
Tomato	Mexico	WP	foliar	1.4-1.9			2
Tomato	Portugal	WP	foliar		0.13		7
Tomato	Spain	WP	foliar		0.13-0.15		10
Watermelon	Honduras	WP	foliar	0.64			3
Watermelon	Mexico	WP	foliar	1.2-1.7			no limit

[1] In some formulations, folpet is mixed with another fungicide which may influence the PHI.
[2] Combination product, 40% folpet + 5% metalaxyl

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue trials reviewed in 1998 (and in a few cases in 1993) have now been re-evaluated in the light of the new information now provided on GAP, and the trials that comply with current GAP are listed in Table 12.

Table 12. Interpretation table for folpet residues in apples, grapes, strawberries, onions, cucumbers, melons, tomatoes, lettuce and potatoes from trials in Tables 13-20 of the 1998 evaluation and Tables 4-7 of the 1993 evaluation. GAP and trial conditions are compared for treatments considered valid for estimation of maximum residue levels and STMRs.

Crop	Country	Use pattern				Trial	Folpet, mg/kg
		kg ai/ha	kg ai/hl	No of appl.	PHI days		
APPLE							
Apple	Argentina GAP		0.12		15		
Apple	Argentina trial	3.6	0.12	3	10	AA950314.07	1.4
Apple	Argentina trial	3.6	0.12	3	10	AA950314.08	2.6
Apple	Chile GAP	2.0	0.11		7		
Apple	Chile trial	2.0	0.11	3	7	AA950314.05	2.0
Apple	Chile trial	2.0	0.11	3	7	AA950314.06	3.7
Apple	Hungary GAP	1.5			10		
Apple	Hungary trial	1.6	0.10	8	10	MAK374-01	8.0
Apple	Portugal GAP		0.13		21		
Apple	[1]Portugal trial	1.3	0.13	10	21	FP/25/91	1.8
Apple	Portugal trial	1.6	0.13	8	21	MAK/374-05	3.2
Apple	Spain GAP		0.15		10		
Apple	Spain trial	1.9	0.16	6	10	MAK/374-04	3.1
Apple	Switzerland GAP		0.08		21		
Apple	Switzerland trial	2.0	0.10	4	21	MAK/374-03	3.4
GRAPES							
Grapes	Argentina GAP		0.13		7		
Grapes	Argentina trial	1.0	0.13	4	7	AA950313.07	1.6
Grapes	Chile GAP	2.0	0.15		14		
Grapes	Chile trial	2.0	0.15	3	14	AA950313.06	2.6
Grapes	Chile trial	2.0	0.15	3	14	AA950313.08	3.0
Grapes	France GAP	1.5			21		
Grapes	France trial	1.5		8	27	R7194	1.9
Grapes	France trial	1.5		7	21	R7194	1.6
Grapes	France trial	1.6	0.50	8	21	R-9146 FR03	2.2
Grapes	France trial	1.4	0.50	8	21	R-9146 FR02	2.4
Grapes	France trial	1.5	0.47	8	21	R-9146 FR01	3.1
Grapes	France trial	1.5	0.60	9	21	R-9146 FR04	2.8
Grapes	France trial	1.9-2.0	0.57-0.76	8	21	R9098	5.8
Grapes	France trial	1.9	0.55-0.78	8	21 (28)[2]	R9098	3.5
Grapes	France trial	1.4-1.6	0.57-0.63	8	21	R9098	1.9
Grapes	France trial	1.6-2.0	0.64-0.84	8	21	R9098	4.6
Grapes	France trial	1.7-1.9	0.49-0.76	8	21	R9098	5.7
Grapes	France trial	1.3-1.6	0.54-0.65	8	21	R9098	5.9
Grapes	[1]France trial	1.5	1.1	7	21	101/91	1.2
Grapes	[1]France trial	1.5	1.9	7	21	103/91	1.3
Grapes	Italy GAP		0.16		10		
Grapes	Italy trial	1.6	0.16	5	10	AA950313.03	3.3
Grapes	[1]Italy trial	1.5	0.15	10	10	IT-301-91	0.58
Grapes	Mexico GAP	1.2			10		

[1] From 1993 JMPR

[2] The residue on day 28 (3.5 mg/kg) exceeded the residue on day 21 (2.6 mg/kg).

Crop	Country	Use pattern				Trial	Folpet, mg/kg
		kg ai/ha	kg ai/hl	No of appl.	PHI days		
Grapes	Mexico trial	1.0	0.14	7	10	AA950313.05	<0.05
Grapes	Spain GAP		0.20		21		
Grapes	[1]Spain trial	0.8	0.2	3	20	SP-201-91	2.0
STRAWBERRY							
Strawberries	Spain GAP		0.15		21		
Strawberries	Italy trial	0.89	0.15	3	21	R-8989	<0.01
Strawberries	Italy trial	0.76	0.13	3	21	R9093	0.04
Strawberries	Italy trial	0.75	0.13	3	21	R9383	0.09
Strawberries	[1]Spain trial	1.29	0.15	4	21		1.1
Strawberries	Mexico GAP	1.2			2		
Strawberries	Mexico trial	1.2	0.62	4	2	950310.01	1.8
Strawberries	Mexico trial	1.2	0.26	4	2	950310.02	1.6
Strawberries	Mexico trial	1.2	0.33	4	2	950310.03	2.2
Strawberries	Netherlands GAP		0.13	g	14		
Strawberries	Netherlands trial	1.4	0.13	2 pt	14	MAK/372.01	1.9
Strawberries	Netherlands trial	1.3	0.13	2 pt	14	MAK/372.01	1.6
Strawberries	Netherlands trial	1.3	0.13	2 pt	14	MAK/372.02	1.4
ONION							
Onions	Chile GAP	2.0	0.13		7		
Onions	Chile trial	2.0	0.13	3	7	AA950307.03	0.36
Onions	Greece GAP		0.16		20		
Onions	Greece trial	0.62	0.12	3	20	MAK/377-07	<0.05
Onions	Greece trial	0.62	0.12	3	20	MAK/377-06	<0.05
Onions	Hungary GAP		0.13		14		
Onions	Hungary trial	0.65	0.13	3	14	MAK/377-02	0.07
Onions	Hungary trial	0.65	0.13	3	14	MAK/377-03	<0.05
Onions	Hungary trial	0.67	0.13	3	14	MAK/377-04	0.21
Onions	Hungary trial	0.65	0.13	3	14	MAK/377-01	0.05
Onions	Mexico GAP	1.4			7		
Onions	Mexico trial	1.5	0.51	4	7	AA950307.01	0.41
Onions	Mexico trial	1.5	0.56	4	7	AA950307.02	0.41
Onions	Portugal GAP		0.13		7		
Onions	Portugal trial	0.54	0.13	3	7	MAK/377-08	5.0
Onions	Spain trial	0.65	0.16	3	10	MAK/377-09	2.5
CUCUMBER							
Cucumber	Cyprus GAP	1.0	0.1		2		
Cucumber	Cyprus trial	1.2	0.12	6	3	CY002/93	0.11
Cucumber	Hungary GAP		0.13		14		
Cucumber	Hungary trial	1.3	0.13	2	14	2/94	<0.02
Cucumber	Mexico GAP	1.7			3		
Cucumber	Mexico trial	1.8	0.50	4	3	AA950312.04	0.11
Cucumber	Mexico trial	1.7	0.76	4	3	AA950312.03	0.36
Cucumber	Mexico trial	1.8	0.67	4	3	AA950312.01	0.70
Cucumber	Mexico trial	1.8	0.79	4	3	AA950312.02	0.56
MELON							
Melons	Greece GAP		0.16		20		
Melons	Greece trial	0.98	0.12	4	20	MAK/373-01	<0.05
Melons	Greece trial	0.97	0.12	4	20	MAK/373-02	<0.05
Melons	Honduras GAP	0.64	0.16		3		

Crop	Country	Use pattern				Trial	Folpet, mg/kg
		kg ai/ha	kg ai/hl	No of appl.	PHI days		
Melons	Guatemala trial	0.49	0.10	6	3	AA950308.06	0.23
Melons	Honduras trial	0.65	0.13	4	3	AA950308.04	0.32
Melons	Honduras trial	0.65	0.13	4	3	AA950308.05	0.41
Melons	Mexico GAP	1.7			7		
Melons	Mexico trial	1.8	0.79	6	7	AA950308.01	2.2
Melons	Mexico trial	1.8	0.55	6	7	AA950308.02	0.89
Melons	Mexico trial	1.8	0.63	6	7	AA950308.03	0.40
TOMATO							
Tomato	Chile GAP	1.9	0.15		7		
Tomato	Chile trial	1.7	1.5	7	7	R-9141t	2.4
Tomato	Hungary GAP		0.13		14		
Tomato	Hungary trial	0.65	0.13	3	14	MAK/375.01	<0.05
Tomato	Hungary trial	0.65	0.13	3	14	MAK/375.04	<0.05
Tomato	Hungary trial	0.65	0.13	3	14	MAK/375.02	<0.05
Tomato	Hungary trial	0.66	0.13	3	14	MAK/375.03	<0.05
Tomato	[1]Hungary trial	0.63	0.12	5	14	FP/26/91	<0.02
Tomato	Mexico GAP	1.9			2		
Tomato	Mexico trial	2.0	0.67	5	2	AA950311.01	1.0
Tomato	Mexico trial	2.0	0.71	5	2	AA950311.04	1.6
Tomato	Mexico trial	2.0	0.66	5	2	AA950311.05	1.8
Tomato	Mexico trial	2.0	0.71	5	2	AA950311.02	0.45
Tomato	Mexico trial	2.0	0.72	5	2	AA950311.03	1.3
Tomato	Portugal GAP		0.13		7		
Tomato	Portugal trial	1.3	0.16	4	7	MAK/375.08	0.34
Tomato	Portugal trial	1.3	0.16	4	7	MAK/375.09	0.58
Tomato	Spain GAP		0.15		10		
Tomato	Italy trial	1.2	0.13	4	10	R-8987	0.60
Tomato	Italy trial	1.3	0.13	4	10	ERSA-DA-14/96	0.70
Tomato	Italy trial	1.3	0.13	4	10 (14)[3]	ERSA-DA-08/96	0.80
Tomato	Italy trial	1.2	0.13	4	10	ERSA-DA-11/95	0.43
Tomato	Spain trial	1.6	0.20	6	10	MAK/375.06	1.3
Tomato	Spain trial	2.5	0.16	6	10	MAK/375.07	1.2
LETTUCE							
Lettuce	Hungary GAP		0.13		14		
Lettuce, Head	Hungary trial	0.66	0.13	pt 3	14	MAK/378-01	24
Lettuce, Head	Hungary trial	0.67	0.13	pt 3	14	MAK/378-02	29
Lettuce, Head	Hungary trial	0.65	0.13	pt 3	14	MAK/378-04	12
Lettuce, Head	Hungary trial	0.66	0.13	pt 3	14	MAK/378-03	39
Lettuce, Head	Hungary trial						
Lettuce	Mexico GAP	1.2			7		
Lettuce, Head	Mexico trial	1.3	0.44	5	7	AA950309.03	4.5
Lettuce, Head	Mexico trial	1.3	0.40	5	7	AA950309.02	9.8
Lettuce, Head	Mexico trial	1.3	0.46	5	7	AA950309.04	16
Lettuce	Portugal GAP		0.13		14		

[3] The residue on day 14 (0.80 mg/kg) exceeded the residue on day 10 (0.62 mg/kg).

Crop	Country	Use pattern				Trial	Folpet, mg/kg
		kg ai/ha	kg ai/hl	No of appl.	PHI days		
Lettuce, Head	Portugal trial	0.52	0.13	3	14	MAK/378-09	4.3
POTATO							
Potato	Spain GAP		0.15		10		
Potato	Italy trial	1.3	0.13	4	10	R8988	0.08
Potato	Italy trial	1.2	0.13	3	10	R9094	<0.01
Potato	Italy trial	1.3	0.13	3	10	R9261	<0.01
Potato	Italy trial	1.3	0.13	4	10	R9374	<0.01
Potato	Mexico GAP	1.9			30		
Potato	Mexico trial	2.4	0.48	5	30	AA960303	0.01
Potato	Mexico trial	5.2	0.96	5	30	AA960303	0.01
Potato	Mexico trial	2.5	0.61	5	30	AA960303	<0.01
Potato	Mexico trial	4.8	1.2	5	30	AA960303	<0.01
Potato	Ukraine GAP	1.5			20		
Potato	Poland trial	1.6		3	21	R9711	<0.01
Potato	Russia trial	1.5	0.5	3	12	R9772	<0.1
Potato	Russia trial	1.5	0.38	3	12	R9772	<0.1
Potato	Russia trial	1.5	0.38	3	20	R9790	<0.04
Potato	Russia trial	1.5	0.38	3	20	R9790	<0.04

g: glasshouse use pt: plastic tunnel use

APPRAISAL

Folpet was evaluated in 1998 for residues in the CCPR Periodic Review Programme. The 1998 Meeting did not receive information on the environmental fate of folpet in soil and in water/sediment systems and (1) agreed that its estimates of maximum residue levels should not be recommended for use as MRLs and (2) recommended withdrawal of existing draft MRLs until these critical supporting studies could be evaluated.

The 1998 Meeting noted that farm animal feeding studies had not been provided, but would be needed before MRLs could be recommended for cereal grain, fodder and forage. The Meeting re-examined this requirement in the light of the results of a metabolism study in which goats had been dosed with [^{14}C]folpet at the equivalent of 24 ppm in the feed for 6 days. Folpet itself was not present in the milk and tissues, but metabolites were identified at levels of 0.001-0.02 mg/kg.

The FAO Manual (Chapter 3.1.5.1) states that livestock processing studies are required where significant residues (>0.1 mg/kg) occur in commodities fed to animals and where significant residues (>0.01 mg/kg) may occur in edible tissues. The Meeting agreed that the metabolism study satisfied the need for a ruminant feeding study up to the feed level tested because no significant residues occurred in the tissues. The Meeting noted that no studies of poultry metabolism had been evaluated.

The Meeting received information on the environmental fate of folpet in soil and on aqueous hydrolysis and photolysis which satisfied the requirements for these critical supporting studies. A study of potato metabolism was also made available.

The metabolism of folpet applied to the foliage of potatoes was similar to that in other plants with the main metabolites in the tubers identified as phthalic and phthalamic acids. Folpet itself was not translocated into the tubers.

The disappearance of folpet incubated with soil under aerobic conditions was biphasic, with initial half-lives of below 10 days but with extended half-lives in the longer term. Phthalimide was the only major degradation product. Half of the folpet was mineralized in the first month.

The estimated half-life of folpet in anaerobic soil was 15 days.

In a field dissipation study folpet and phthalimide were detected mainly in the surface soils and had disappeared within one week of the final treatment. Folpet and its soil degradation products showed low mobility in a soil column leaching study.

The half-lives of folpet dissolved at 1 mg/l in sterile aqueous buffered solutions at 25°C in the dark were 2.6 hours, 1.1 hours and 67 seconds at pH 5, 7 and 9 respectively. Hydrolysis at pH 3 was not accelerated by exposure to natural sunlight or a UV lamp, showing that photolysis played little part in breakdown.

Folpet itself disappeared very quickly from a water/sediment system incubated in the dark, as would be expected from its rate of abiotic hydrolysis. The study was recently completed and a brief summary was provided.

Residue trials were reviewed in 1998. New information has now been provided on GAP, which has assisted re-evaluation. Current GAP and relevant data from the supervised trials are summarized in an interpretation table in the 1999 Evaluation.

Apples. Folpet is registered in Argentina for use on apples with a spray concentration of 0.12 kg ai/hl and a PHI of 15 days. The residues in apples from 2 trials where the spray concentration matched GAP but the PHI was 10 days (sufficiently close for a persistent residue) were 1.4 and 2.6 mg/kg.

In two trials in Chile where the conditions corresponded to Chilean GAP (2.0 kg ai/ha and PHI 7 days) the residues were 2.0 and 3.7 mg/kg.

In a Hungarian trial according to GAP (application at 1.6 kg ai/ha and a PHI of 10 days) the folpet residue on apples was 8.0 mg/kg. In a Swiss trial according to GAP (spray concentration 0.10 kg ai/hl and a PHI of 21 days) the residue was 3.4 mg/kg, and in a Spanish trial also according to GAP (spray concentration 0.16 kg ai/hl and a PHI of 10 days) the residue was 3.1 mg/kg.

Folpet may be sprayed at 0.13 kg ai/hl on apples in Portugal with harvest 21 days after the final application. In a trial meeting these conditions the residue was 3.2 mg/kg. In a trial recorded in the 1993 Evaluations folpet was applied 10 times at a concentration of 0.13 kg ai/hl and the resulting residue 21 days after the final application was 1.8 mg/kg

In summary, the residues in apples from trials according to GAP were Argentina 1.4, 2.6 mg/kg, Chile 2.0, 3.7 mg/kg, Hungary 8.0 mg/kg, Switzerland 3.4 mg/kg, Spain 3.1 mg/kg and Portugal 1.8, 3.2 mg/kg. The residues in rank order (median underlined) in the 9 trials were 1.4, 1.8, 2.0, 2.6, 3.1, 3.2, 3.4, 3.7 and 8.0 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 3.1 mg/kg for folpet on apples. The estimated maximum residue level supports the existing draft MRL.

Grapes. In two trials in Chile corresponding to Chilean GAP (2.0 kg ai/ha and PHI 14 days) the residues were 2.6 and 3.0 mg/kg, and in a Mexican trial according to GAP (1.0 kg ai/ha, PHI 10 days) the residue was <0.05 mg/kg.

In 12 French trials according to GAP (1.5 kg ai/ha and 21 days PHI) the residues were 1.6, 1.9, 1.9, 2.2, 2.4, 2.8, 3.1, 3.5, 4.6, 5.7, 5.8 and 5.9 mg/kg.

The 1993 JMPR reported 4 trials according to national GAP, 2 French (1.5 kg ai/ha, PHI 21 days), 1 Italian (0.16 kg ai/hl, 10 days PHI) and 1 Spanish (0.20 kg ai/hl, 21 days PHI). The residues were 1.2, 1.3, 0.58 and 2.0 mg/kg respectively.

The trial in Mexico may have been from a different population and was excluded from the evaluation.

In summary, the residues in grapes from trials according to GAP were Argentina 1.6 mg/kg, Chile 2.6, 3.0 mg/kg, France 1.2, 1.3, 1.6, 1.9, 1.9, 2.2, 2.4, 2.8, 3.1, 3.5, 4.6, 5.7, 5.8 and 5.9 mg/kg, Italy 0.58, 3.3 mg/kg and Spain 2 mg/kg. The residues in rank order (median underlined) in the 20 trials were 0.58, 1.2, 1.3, 1.6, 1.6, 1.9, 1.9, 2.0, 2.2, 2.4, 2.6, 2.8, 3.0, 3.1, 3.3, 3.5, 4.6, 5.7, 5.8 and 5.9 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 2.5 mg/kg for folpet on grapes. The estimated maximum residue level supports the existing draft MRL.

Strawberries. Folpet is registered in Spain at a spray concentration of 0.15 kg ai/hl and a PHI of 21 days. The residues were <0.01, 0.04 and 0.09 mg/kg in three trials in Italy and 1.1 mg/kg in one Spanish trial (1993 JMPR) according to Spanish GAP.

Mexican GAP permits application of folpet to strawberries at 1.3 kg ai/ha 2 days PHI. The residues in 3 Mexican trials complying with GAP were 1.6, 1.8 and 2.2 mg/kg.

In 3 trials in plastic tunnels according to glasshouse GAP in The Netherlands (spray concentration of 0.13 kg ai/hl and 14 days PHI) the residues were 1.4, 1.6 and 1.9 mg/kg.

In summary, the residues in strawberries from trials according to GAP were Italy <0.01, 0.04 and 0.09 mg/kg, Mexico 1.6, 1.8 and 2.2 mg/kg, The Netherlands 1.4, 1.6 and 1.9 mg/kg and Spain 1.1 mg/kg. The Meeting agreed that the residues in Italy appeared to be a different population from the others and should be excluded. The residues in rank order (median underlined) in the remaining 7 trials were 1.1, 1.4, 1.6, 1.6, 1.8, 1.9 and 2.2 mg/kg.

The Meeting estimated a maximum residue level of 5 mg/kg and an STMR of 1.6 mg/kg for folpet on strawberries. The estimated maximum residue level supports the existing draft MRL.

Onions. The residue in onions from a trial in Chile in accordance with GAP (application of 2 kg ai/ha and 7 days PHI) was 0.36 mg/kg. The residues in 2 trials in Mexico (application at 1.5 kg ai/ha) were 0.41 and 0.41 mg/kg with conditions complying with GAP (1.4 kg ai/ha and 7 days PHI).

Portuguese GAP for onions allows a folpet spray concentration of 0.13 kg ai/hl and a 7 days PHI. The residues in one trial in Portugal and one in Spain (0.16 kg/hl, PHI 10 days) complying with this were 5.0 and 2.5 mg/kg respectively. Two trials in Greece (0.12 kg ai/hl and 20 days PHI) were acceptably close to Greek GAP (0.16 kg ai/hl with a 20 days PHI) and produced no detectable residues (<0.05 mg/kg).

Four Hungarian trials according to Hungarian GAP (0.13 kg ai/hl and 14 days PHI) produced residues of <0.05, 0.05, 0.07 and 0.21 mg/kg.

In summary, the residues in onions from trials according to GAP were Chile 0.36 mg/kg, Greece <0.05, <0.05 mg/kg, Hungary <0.05, 0.05, 0.07 and 0.21 mg/kg, Mexico 0.41, 0.41 mg/kg, Portugal 5.0 mg/kg and Spain 2.5 mg/kg. The Meeting agreed that the residues in the Portuguese and Spanish trials appeared to be from a different population from the remainder and that only 9 trials would be used for the evaluation. The residues in onions in rank order (median underlined) in the 9 trials were <0.05 (3), 0.05, 0.07, 0.21, 0.36, 0.41 and 0.41 mg/kg.

The Meeting noted that the three highest values suggested that residues would sometimes exceed 0.5 mg/kg and estimated a maximum residue of 1 mg/kg and an STMR of 0.07 mg/kg for folpet in onions.

Cucumbers. In Cyprus folpet is registered for use on cucumbers at 1.0 kg ai/ha with a 2 days PHI. The residues in cucumbers were 0.11 mg/kg in a Cyprus trial sufficiently close to GAP (1.2 kg ai/ha and 3 days PHI).

In Hungary the residues in cucumbers were <0.02 mg/kg in a trial according to Hungarian GAP (0.13 kg ai/hl and 14 days PHI).

Folpet may be used on cucumbers in Mexico at 1.7 kg ai/ha with a 3 days PHI. In the 4 trials in Mexico according to GAP the residues were 0.11, 0.36, 0.56 and 0.70 mg/kg.

A Canadian trial could not be used because the trial conditions (application rate 1.0 kg ai/ha and spray concentration 0.10 kg ai/hl) did not match maximum GAP (2.0 kg ai/ha, 0.20 kg ai/hl)

In summary the residues in cucumbers from trials according to GAP were Cyprus 0.11 mg/kg, Hungary <0.02 mg/kg and Mexico 0.11, 0.36, 0.56 and 0.70 mg/kg. The trial in Hungary may have been from a different population and was excluded from the evaluation. The residues in rank order (median underlined) in the 5 trials were 0.11, 0.11, 0.36, 0.56 and 0.70 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.36 mg/kg for folpet in cucumbers. The estimated maximum residue level is recommended to replace the draft MRL of 0.5 mg/kg.

Melons. In Greece folpet is registered for use on melons with a spray concentration of 0.16 kg ai/hl and a PHI of 20 days. The residues were below the LOD (<0.05 mg/kg) in melons from 2 Greek trials meeting these conditions (0.12 kg ai/hl and 20 days PHI).

Honduras permits a spray concentration of 0.16 kg ai/hl and harvest 3 days after the final application. Melons were harvested 3 days after the final application in one trial in Guatemala (0.10 kg ai/hl) and 2 trials in Honduras (0.13 kg ai/hl) where the residues were 0.23, 0.32 and 0.41 mg/kg.

Mexican GAP permits application of folpet to melons at 1.8 kg ai/ha and harvest 7 days later. The residues were 0.40, 0.89 and 2.2 mg/kg in melons from 3 Mexican trials according to GAP.

In summary, the residues in melons from relevant trials were Greece <0.05, <0.05 mg/kg, Guatemala 0.23 mg/kg, Honduras 0.32, 0.41 mg/kg and Mexico 0.40, 0.89, 2.2 mg/kg. The trials in Greece may have been from a different population and were excluded from the evaluation. The residues in rank order (median underlined) in the 6 trials were 0.23, 0.32, 0.40, 0.41, 0.89 and 2.2 mg/kg.

The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.41 mg/kg for folpet in melons. The estimated maximum residue level supports the draft MRL.

Tomatoes. Data were available from supervised trials according to GAP in Chile, Hungary, Italy, Mexico, Portugal and Spain. Trials in the USA and The Netherlands and trials in plastic greenhouses in Italy could not be evaluated because no relevant GAP was reported. The evaluated trials were as follows.

The residue in a trial in Chile (application rate 1.7 kg ai/ha, GAP 1.9 kg ai/ha and 7 days PHI) was 2.4 mg/kg.

In Hungary folpet is registered for use on tomatoes at a spray concentration of 0.13 kg ai/hl with harvest permitted 14 days after the final application. In 4 Hungarian tomato trials reported in 1998 and 1 reported in 1993, the residues were all below the LOD (<0.02 and <0.05 mg/kg).

Mexican GAP permits application of folpet to tomatoes at 1.9 kg ai/ha and harvest 2 days later. The residues from 5 Mexican trials were 0.45, 1.0, 1.3, 1.6 and 1.8 mg/kg.

In 2 Portuguese trials (0.16 kg ai/hl and 7 days PHI) in compliance with Portuguese GAP (0.13 kg ai/hl and 7 days PHI) the residues were 0.34 and 0.58 mg/kg.

The registered use in Spain permits a spray concentration of 0.15 kg ai/hl and a 10 days PHI. The residues in 2 Spanish and 4 Italian trials in substantial agreement with Spanish GAP were 1.2 and 1.3 mg/kg in Spain and 0.43, 0.60, 0.70 and 0.80 mg/kg in Italy.

In summary, the residues in tomatoes from the relevant trials were Chile 2.4 mg/kg, Mexico 0.45, 1.0, 1.3, 1.6, 1.8 mg/kg, Hungary <0.02, <0.05 4 mg/kg, Portugal 0.34, 0.58 mg/kg, Spain 1.2, 1.3 mg/kg and Italy 0.43, 0.60, 0.70, 0.80 mg/kg. The residues in tomatoes in rank order in the 19 trials were <0.02, <0.05 (4), 0.34, 0.43, 0.45, 0.58, 0.6, 0.7, 0.80, 1.0, 1.2, 1.3, 1.3, 1.6, 1.8 and 2.4 mg/kg

The residues from the Hungarian trials appear to be a different population from the others. The residues in the remaining 14 trials (median underlined) were 0.34, 0.43, 0.45, 0.58, 0.6, 0.7, 0.80, 1.0, 1.2, 1.3, 1.3, 1.6, 1.8 and 2.4 mg/kg

The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.90 mg/kg for folpet in tomatoes. The estimated maximum residue level supports the draft MRL.

Head lettuce. Eight trials according to national GAP were reported.

Four trials in plastic tunnels in Hungary (0.13 kg ai/hl and 14days PHI) produced residues of 12, 24, 29 and 39 mg/kg. The residues in 3 Mexican trials (1.3 kg ai/ha and 7 days PHI) were 4.5, 9.8 and 16 mg/kg. The residue from a trial in Portugal in accordance with GAP (0.13 kg ai/hl spray and 14 days PHI) was 4.3 mg/kg.

In summary, the residues in head lettuce from the 8 trials were Hungary 12, 24, 29 and 39 mg/kg, Mexico 4.5, 9.8 and 16 mg/kg and Portugal 4.3 mg/kg. The residues in rank order (median underlined) were 4.3, 4.5, 9.8, 12, 16, 24, 29 and 39 mg/kg.

The Meeting estimated a maximum residue level of 50 mg/kg and an STMR of 14 mg/kg for folpet in head lettuce.

Potatoes. Supervised trials on potatoes were reported from Italy, Mexico, Poland, Russia and South Africa. Translocation of folpet to the tubers from foliar application would not be expected from such a water-insoluble compound as folpet, and this was borne out by the potato metabolism study. Occasional residues could occur if a tuber is exposed above the soil surface to direct spray.

Spanish GAP (spray concentration 0.15 kg ai/hl and PHI 10 days) was used to evaluate 4 Italian trials (0.13 kg ai/hl, 10 days PHI) where the residues were 0.08 and <0.01 (3) mg/kg.

Mexican GAP specifies application at 1.9 kg ai/ha with harvest 30 days later. The residues in potatoes were below the LOD (0.01 mg/kg) in 2 trials with application rates of 2.5 and 4.8 kg ai/ha and were 0.01 mg/kg in 2 trials with application rates of 2.4 and 5.2 kg ai/ha. Trials with exaggerated rates can be included in the evaluation because the chance of residues occurring depends more upon spray contacting exposed tubers than upon the application rate.

GAP in the Ukraine allows application of 1.5 kg ai/ha with 20 days PHI. Trials in Poland and Russia were evaluated against Ukrainian GAP. The residues in one Polish and 4 Russian trials where application was at 1.5-1.6 kg ai/ha with harvest 12-21 days later were <0.01, <0.04 (2) and <0.1 mg/kg.

In summary, the residues in potatoes from the 13 trials effectively according to GAP were Italy <0.01 (3), 0.08 mg/kg, Mexico <0.01 (2), 0.01 mg/kg (2), Poland <0.01 mg/kg and Russia <0.04 (2), <0.1 mg/kg (2). The residues in rank order (median underlined) were <0.01 (6), <u>0.01</u> (2), 0.04 (2) 0.08 and <0.1 (2) mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.01 mg/kg for folpet in potatoes.

<u>Processing</u>

The 1998 JMPR reported processing factors of 2.6 and 0.035 for wet apple pomace and apple juice respectively. The Meeting estimated STMRs of 8.1 mg/kg (2.6 x 3.1) for wet pomace and 0.11 mg/kg (0.035 x 3.1) for juice.

The 1998 Meeting reported a processing factor of 3.2 for producing dried grapes (raisins) and estimated a maximum residue level of 40 mg/kg for folpet residues in dried grapes. The Meeting confirmed this estimate, which agrees with the existing draft MRL. By applying the processing factor (3.2) to the STMR for grapes (2.5 mg/kg) the Meeting estimated an STMR of 8.0 mg/kg for dried grapes. The same processing factor applied to the HR found in the trials on grapes (5.9 mg/kg) produced an HR-P of 18.9 mg/kg for dried grapes (raisins).

The calculated processing factor for grape juice was 0 (<0.003); folpet was not detected in the juice. The Meeting estimated an STMR for grape juice of 0.0075 mg/kg (0.003 x 2.5).

Folpet was not detected (<0.05 mg/kg) in wine in 10 processing trials, providing good evidence that the residues do not occur in wine, which is implied by the rapid hydrolysis of folpet in solution and the removal of insolubles in the process and that the processing factor for wine is 0. The Meeting estimated an STMR of 0 mg/kg for folpet residues in wine.

The calculated processing factor for the transfer of the residues from tomatoes to purée and paste is 0 (<0.028); residues in the processed commodities were below the LOD, 0.05 mg/kg. The Meeting estimated STMRs of 0.025 mg/kg (0.028 x 0.90) for tomato purée and paste.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue (for compliance with MRLs and for the estimation of dietary intake): folpet.

Commodity		MRL, mg/kg		STMR, mg/kg	HR or HR-P[1],
CCN	Name	New	Previous		mg/kg

Commodity		MRL, mg/kg		STMR, mg/kg	HR or HR-P[1], mg/kg
CCN	Name	New	Previous		
FP 0226	Apple	10	10[2]	3.1	8.0
JF 0226	Apple juice			0.11	
	Apple pomace, wet			8.1	
VC 0424	Cucumber	1	0.5[3]	0.36	0.70
DF 0269	Dried grapes (Currants, Raisins and Sultanas	40	40[2]	8.0	18.9
FB 0269	Grapes	10	10[2]	2.5	5.9
JF 0269	Grape juice			0.0075	
VL 0482	Lettuce, Head	50	-	14	39
VC 0046	Melons, except watermelon	3	3[3]	0.41	2.2 [4]
VA 0385	Onion, Bulb	1	-	0.07	0.41
VR 0589	Potato	0.1	0.02*[3]	0.01	0.08
FB 0275	Strawberry	5	5[2]	1.6	2.2
VO 0448	Tomato	3	3[2]	0.90	2.4
	Tomato paste			0.025	
	Tomato purée			0.025	
	Wine			0	

[1]HR: highest residue (edible portion) from supervised trials. HR-P: highest residue in the processed commodity, calculated from the HR of the raw agricultural commodity and the processing factor.
[2]The 1998 JMPR recommended withdrawal because critical supporting studies on the environmental fate of folpet were not provided.
[3]The 1998 JMPR recommended withdrawal because there were too few appropriate residue trials.
[4]Melons HR is expressed on a whole fruit basis.

DIETARY RISK ASSESSMENT

Chronic intake

New and revised MRLs for folpet have been recommended for apples, cucumbers, dried grapes, grapes, head lettuce, melons, onion, potato, strawberry and tomato. STMRs have been estimated for the primary commodities and some processed commodities. The dietary intake of folpet is shown in Annex III.

International Estimated Daily Intakes for folpet for the 5 GEMS/Food regional diets, based on estimated STMRs, were in the range of 0-9% of the ADI. The Meeting concluded that the intake of

residues of folpet resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The international estimate of short-term intake (IESTI) for folpet was calculated as described in Section 3 of this report for commodities for which MRLs were recommended and STMRs estimated and for which consumption data (large portion consumption, unit weight) were available. The results are shown in Annex IV. The IESTI ranged from 0 to 0.15 mg/kg bw in the total population and from 0 to 0.49 mg/kg bw in children. As no acute reference dose has been established, the acute risk assessment for folpet was not finalized.

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GLUFOSINATE-AMMONIUM (175)

EXPLANATION

Glufosinate-ammonium is a herbicide or desiccant. It was first evaluated for residues and toxicology by the 1991 JMPR and subsequently for residues in 1994 and 1998. The 1998 JMPR evaluated trials with glufosinate-ammonium on glufosinate-tolerant crops.

The current definition of the glufosinate residue includes glufosinate and 3-[hydroxy(methyl)phosphinoyl]propionic acid (MPP) and is based on the residues occurring in conventional crops. When glufosinate is used on genetically modified glufosinate-tolerant crops *N*-acetyl-glufosinate (NAG) is produced as a major part of the residue. The 1998 JMPR considered a revised residue definition, but could not recommend its use until the toxicological evaluation of NAG had been completed. This has now been done.

In the use of glufosinate-ammonium on glufosinate-tolerant canola in Canada, the timing of the final application is specified at the early bolting growth stage. The Meeting received new information on the interpretation of 'early bolting.'

Definition of the residue

The 1998 JMPR suggested a revised residue definition to take into account the nature of the residue occurring in conventional and transgenic glufosinate-tolerant crops: "sum of glufosinate-ammonium, 3[hydroxy(methyl)phosphinoyl]propionic acid and *N*-acetyl-glufosinate, expressed as glufosinate (free acid)".

When glufosinate is used on genetically modified glufosinate-tolerant crops NAG is produced (Figure 1). It should be included in the residue definition for enforcement because (1) it is sometimes the major residue component, and (2) the same GLC derivative is produced in the analytical method from both glufosinate itself and NAG (Figure 2), so unless the compounds are separated before derivatization they both appear as their common derivative.

The revised definition is also suitable for commodities from conventional crops because if NAG is absent it will not contribute to the analytical result and if present at low levels it is necessarily already included in the analytical result. NAG is a minor metabolite or degradation product in animals, soils and water/sediment systems.

In the light of the current toxicological evaluation of NAG the Meeting confirmed the suggested residue definition as suitable both for compliance with MRLs and for the estimation of dietary intake.

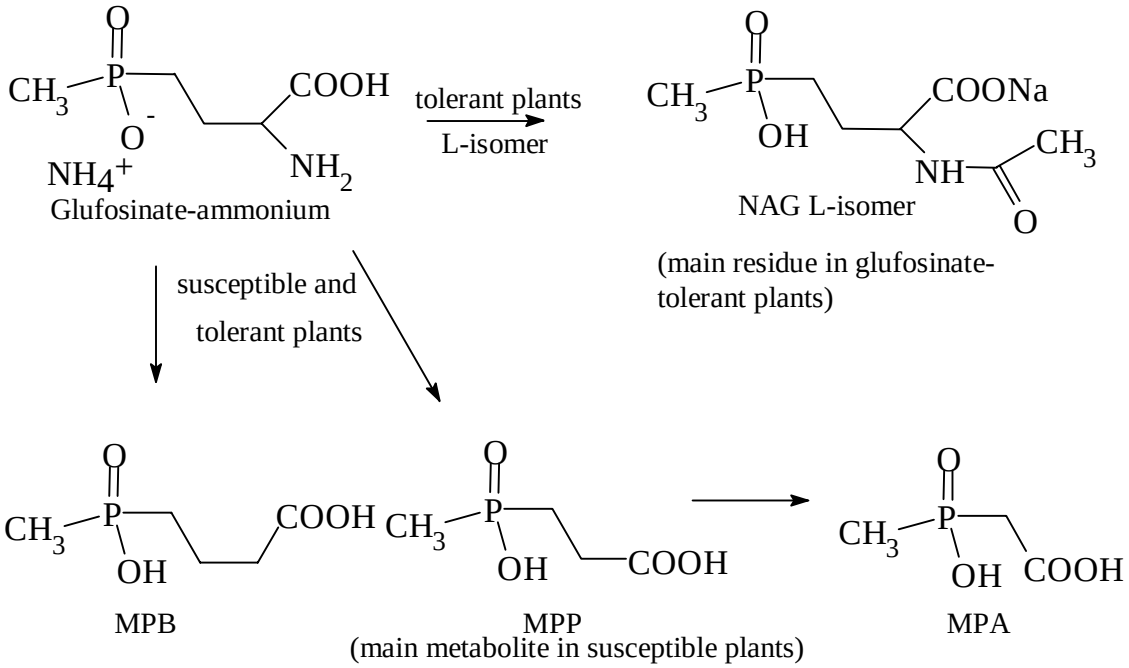


Figure 1. Proposed metabolic pathways of glufosinate-ammonium in plants.

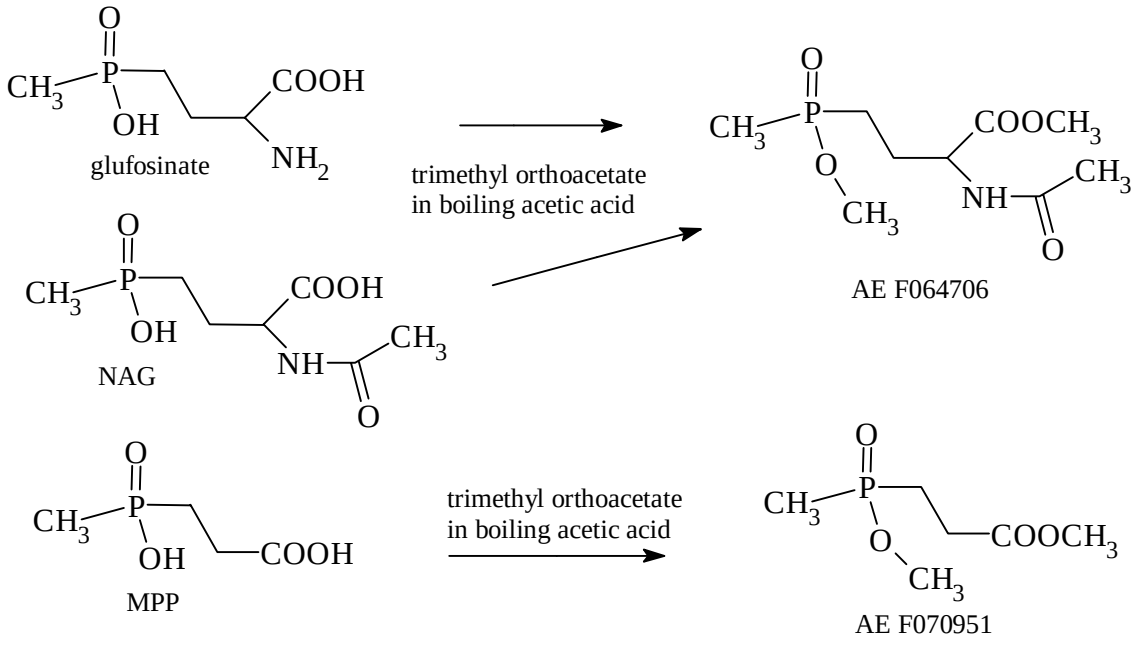


Figure 2. Derivatization of glufosinate and metabolites for determination of residues by GLC.

USE PATTERN

The registered use pattern for glufosinate-ammonium on tolerant canola in Canada shown below (Table 1) is extracted from the Table of registered uses in the 1998 Residue Evaluations.

Table 1. Registered uses of glufosinate-ammonium. Concentrations and rates are expressed in terms of the active ingredient glufosinate-ammonium.

Crop	Country	Form	Application			Number	Growth stage
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl		
Canola (tolerant)	Canada	150 g/l SL	foliar	0.30-0.50	min spray vol 110 l/ha	2	early bolting
Canola (tolerant)	Canada	150 g/l SL	foliar	0.60	min spray vol 110 l/ha	1	early bolting

MacDonald *et al.* (1999) have provided a detailed explanation of 'early bolting'. The Canola Council divides the growth of canola into 6 stages: 0 pre-emergence, 1 seedling, 2 rosette, 3 bud, 4 flower, and 5 ripening. The bud stage is where the flower cluster becomes visible in the centre of the rosette. The formation of the flower buds is accompanied by rapid stem elongation (bolting). Plants at the 5-6 leaf stage under Canadian conditions are likely to be in the bud or early bolting phase of development. It is typical to have several growth stages present simultaneously in a trial, so the growth stage is given as a range. It is possible to have plants in both the rosette and bud stages in a trial where the growth stage is given as 4-6 leaf.

There are two reasons for the discrepancy between the interpretation of the leaf stage for early bolting in oilseed rape in the EU (10 leaf stage) and in Canada. The first is that oilseed rape is sown in the autumn in the EU and the plants require a vernalization period to initiate flowering; the plant grows in the autumn, but the bud stage will not occur until the following spring. The second is that the hot summer temperatures, low soil moisture and long day length in Western Canada are conducive to the rapid initiation of the bud phase.

RESIDUES RESULTING FROM SUPERVISED TRIALS

In the light of the new information on Canadian GAP the Meeting re-evaluated the Canadian trials on glufosinate-resistant canola reviewed by the 1998 JMPR (Table 2).

Table 2. Interpretation table for glufosinate-ammonium residues in canola in trials in Canada recorded in the 1998 JMPR Residue Evaluations. GAP and trial conditions are compared for trials considered valid for the estimation of maximum residue levels and STMRs.

Country	Application				Trial ref	Glufos + NAG +MPP, mg/kg
	kg ai/ha	kg ai/hl	No.	Growth stage		
Canada GAP	0.60		1	early bolting		
Canada trial	0.5	0.45	1	GS 4-5 leaf	XEN93-29-AB-TC-3 A56394	<0.05
Canada trial	0.75	0.68	1	GS 4-6 leaf	XEN93-29-MB-TC-2 A56394	0.12
Canada trial	0.5	0.45	1	GS 4-5 leaf	XEN93-29-MB-TC-3 A56394	<0.05
Canada trial	0.75	0.68	1	GS 4-5 leaf	XEN93-29-MB-TC-3 A56394	<0.05
Canada trial	0.5	0.45	1	GS 4-5 leaf	XEN93-29-MB-TC-4 A56394	<0.05
Canada trial	0.75	0.68	1	GS 4-5 leaf	XEN93-29-MB-TC-4 A56394	<0.05
Canada trial	0.5	0.45	1	GS 10 leaf	XEN93-29-SK-TC-6 A56394	<0.05
Canada trial	0.75	0.68	1	GS 10 leaf	XEN93-29-SK-TC-6 A56394	<0.05
Canada trial	0.8	0.73	1	GS 5-6 leaf	A56392 Minto	<0.05
Canada trial	0.8	0.73	1	GS 5-7 leaf	A56392 Indian Head	0.24
Canada trial	0.8	0.73	1	GS 4-5 leaf	A56392 Portage la Prairie	0.07
Canada trial	0.8	0.73	1	GS 4-6 leaf	Vauxhall	0.17

Residues in animal commodities

The 1998 JMPR evaluated feeding studies in which lactating dairy cows and laying hens were dosed with glufosinate-ammonium + NAG. The present Meeting estimated the dietary burden of residues for the animals using the diets in Appendix IX of the FAO Manual (Table 3). The calculations based on the MRLs and relevant processing factors provide dietary burdens suitable for estimating maximum residue levels for animal commodities, and those based on STMRs for the feed items allow the estimation of STMRs for animal products.

Table 3. Estimated dietary burden of glufosinate residues for beef and dairy cattle and poultry calculated from existing and proposed MRLs (and processing factors for the oilseed meal, and from STMRs where available. DM is dry matter. MRL/DM and STMR/DM are the MRL and STMR expressed on a dry matter basis. STMRs were not available for the components of the poultry diet so the dietary burdens used for estimating maximum residue levels and STMRs in poultry commodities are the same.

Commodity	MRL, mg/kg[1]	Processing factor[2]	DM, %	MRL/DM, mg/kg	% of diet			Residue in diet, ppm		
					Beef	Dairy	Poultry	Beef	Dairy	Poultry
Maize fodder	10		83	12.05						
Maize forage	5		40	12.50	40	50		5.00	6.25	
Almond hulls	0.5		90	0.56	10	10		0.06	0.06	
Maize	0.1		88	0.11	15	15	70	0.02	0.02	0.08
Sugar beet leaves	0.1		23	0.43	20	10		0.09	0.04	
Sunflower seed	5									
Sunflower seed meal	12	2.4	92	13.04			15	0	0	1.80
Rape seed	5									
Rape seed meal	17.0	3.4	88	19.32	15	15	15	2.90	2.90	2.90
Soya bean dry	2									
Soya bean meal	2.6	1.3	89	2.92				0	0	0
							Total dietary burden	11.0	11.1	4.8
	STMR, mg/kg			STMR/DM, mg/kg						
Maize fodder	0.72		83	0.87						
Maize forage	0.54		40	1.35	40	50		0.54	0.68	
Almond hulls	0		90	0	10	10		0	0	
Maize	0.1		88	0.11	15	15	70	0.02	0.02	0.08
Sugar beet leaves	0.1		23	0.43	10	10		0.04	0.04	
Sunflower seed	5									
Sunflower seed meal	12	2.4	92	13.04			15	0	0	1.80
Rape seed	5									
Rape seed meal	17.0	3.4	88	19.32	15	15	15	2.90	2.90	2.90
Soya bean dry	0.87									
Soya bean meal	1.13	1.3	89	1.27				0	0	0
							Total dietary burden	3.7	3.7	4.8

[1]The "MRLs" for the oilseed meals were derived by multiplying the MRLs for the seeds by the corresponding processing factors

[2]The processing factors were derived from processing studies reported by the 1998 and 1994 JMPRs.

APPRAISAL

The 1998 JMPR evaluated glufosinate-ammonium for its uses on glufosinate-tolerant crops. It estimated a number of maximum residue levels, but could not generally recommend them for use as MRLs or propose a revised residue definition until the toxicological evaluation of the metabolite *N*-acetyl-glufosinate (NAG) had been completed. It suggested a provisional revised definition of the residue to take into account the nature of the residue occurring in both conventional and glufosinate-tolerant crops: "sum of glufosinate-ammonium, 3-[hydroxy(methyl)phosphinoyl]propionic acid and *N*-acetyl-glufosinate, expressed as glufosinate (free acid)".

When glufosinate is used on genetically modified glufosinate-tolerant crops *N*-acetyl-glufosinate is produced. It should be included in the residue definition for enforcement because (1) it is sometimes the main residue component, and (2) the same GLC derivative is produced in the analytical method from both glufosinate itself and NAG, so unless the compounds are separated before derivatisation they both appear as their common derivative. The revised definition is also suitable for commodities from conventional crops because if NAG is absent it will not contribute to the analytical result and if present at low levels it is necessarily already included in the analytical result. NAG is a minor metabolite or degradation product in animals, soils and water/sediment systems.

In the light of the current toxicological evaluation of NAG the Meeting confirmed the suggested residue definition as suitable for both compliance with MRLs and for the estimation of dietary intake.

The residue reported in the supervised trials consists of three components: glufosinate, NAG and 3-[hydroxy(methyl)phosphinoyl]propionic acid (MPP). The method of calculating the total residue was described by the 1998 JMPR and is illustrated by example:

Glufosinate	MPP	NAG	Total
<0.05	<0.05	<0.05	<0.05
<0.05	<0.05	0.06	0.06
0.05	<0.05	0.09	0.14

Canadian GAP for canola specifies treatment at 'early bolting'. The 1998 JMPR was informed that the 10-leaf stage is very close to bolting, but subsequent advice from Canada is that under Canadian conditions and practices a 4-6-leaf growth stage corresponds to early bolting.

Twelve Canadian trials on canola were essentially in accord with Canadian GAP (0.60 kg ai/ha, treatment at early bolting) and produced residues of <0.05 (8), 0.07, 0.12, 0.17 and 0.24 mg/kg.

The Meeting estimated a maximum residue level for glufosinate-ammonium in rape seed of 0.3 mg/kg, but noted that the residues arising from this new use were within the existing CXL of 5 mg/kg, which was based on uses on susceptible rape. It is not possible to estimate an STMR on only part of the residue data.

The dietary burden of glufosinate-ammonium for estimating MRLs for animal commodities is 8.1 and 9.3 ppm for beef and dairy cattle respectively and 4.8 ppm for poultry, calculated from MRLs and proposed MRLs for feed commodities.

The levels of 8.1 and 9.3 ppm are comparable to the 9.1 ppm feeding level in the lactating cow feeding study reported in 1998. Residues were not detected in milk (<0.02 mg/kg) or tissues (<0.05 or <0.1 mg/kg) at this feeding level. Occasional residues were detected in milk (0.02, 0.03 mg/kg) at the next feeding level of 27 ppm, but not in the tissues. The Meeting estimated maximum residue levels at the LODs for meat, offal and milk.

The level of 4.8 ppm is equivalent to the nominal 3.6 ppm feeding level in the feeding study on laying hens. No residues were detected in the tissues or eggs at this feeding level. The Meeting estimated maximum residue levels at the LODs for poultry meat, offal and eggs.

The dietary burdens for estimating STMRs for beef and dairy cattle products are 3.5 and 3.6 ppm respectively, derived from the STMRs for maize forage and almond hulls and MRLs for the other feed commodities.

The residues were below the LOD in the muscle, liver and kidneys at feeding levels of 9.1 and 27 ppm. The Meeting noted that the dietary burden of 3.5-3.6 ppm was much less than the feeding level of 27 ppm and as an approximation assumed that tissue residues would be proportional to dietary intake:

STMR for animal commodity = LOD × (STMR dietary burden) ÷ (feeding level)

STMR for meat = 0.05 × 3.6 ÷ 27 = 0.007 mg/kg (no detections at 27 ppm feeding level)

STMR for edible offal = 0.1 × 3.6 ÷ 27 = 0.014 mg/kg (no detections at 27 ppm feeding level)

STMR for milk = 0.02 × 3.6 ÷ 27 = 0.003 mg/kg (no detections at 27 ppm feeding level)

The Meeting agreed that the calculated STMRs were low enough to be treated as effectively zero and estimated STMRs of 0 for meat, edible offal and milks.

STMRs for poultry feed commodities were not produced in this evaluation. Eggs, poultry meat and poultry edible offal were assigned STMRs equivalent to the LODs.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting concluded that the residue levels listed below are suitable for establishing maximum residue limits and for IEDI assessment.

Definition of the residue (for compliance with MRLs and for the estimation of dietary intake): sum of glufosinate-ammonium, 3-[hydroxy(methyl)phosphinoyl]propionic acid and *N*-acetyl-glufosinate, expressed as glufosinate (free acid).

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
MO 0105	Edible offal (Mammalian)	0.1*	-	0
PE 0112	Eggs	0.05*	-	0.05 [1]
AS 0645	Maize fodder	10	-	0.72
AF 0645	Maize forage	5	0.2	0.54

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
MM 0095	Meat (from mammals other than marine mammals)	0.05*	-	0
ML 0106	Milks	0.02*	-	0
PM 0110	Poultry meat	0.05*	-	0.05 [1]
PO 0111	Poultry, Edible offal of	0.1*	-	0.1 [1]
VD 0541	Soya bean (dry)	2	0.1	0.87

[1]LOD is assigned as STMR level.

DIETARY RISK ASSESSMENT

Chronic intake

A revised maximum residue level for glufosinate-ammonium in soya beans and new maximum residue levels in animal commodities together with corresponding STMRs were estimated and combined with existing CXLs and draft MRLs to estimate the dietary intakes shown in Annex III.

Estimated Dietary Intakes for the 5 GEMS/Food regional diets, based on estimated STMRs and existing MRLs, were in the range of 3-10% of the ADI. The Meeting concluded that the intake of residues of glufosinate-ammonium resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The Meeting concluded that an acute RfD for glufosinate-ammonium is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard and residues are therefore unlikely to present an acute risk to consumers

REFERENCES

MacDonald, R., Sonder, K. and Stumpf, K. 1999. Canola residue trials. Further information on canola growth stages. Canola grown under North American (Canadian) conditions. Report PSR99/016. Hoechst Schering AgrEvo GmbH, Germany. Unpublished.

MALATHION (049)

EXPLANATION

Malathion is an insecticide used world wide in a large number of fruit, vegetables and cereal crops. It was originally scheduled for periodic re-evaluation by the 1995 JMPR. The review was postponed at the 1994 CCPR as the manufacturer informed the meeting that a long term study would not be available before the end of 1995 (ALINORM 95/24, para 115). It was re-scheduled for periodic re-evaluation of residues by the 1999 JMPR at the 1995 CCPR (ALINORM 95/24A, Appendix IV). The manufacturer provided residue data, GAP information and relevant critical supporting studies to support existing CXLs. Relevant data have also been provided in support of residue limits for alfalfa, asparagus, avocado, snap beans, carrot, clover, corn, cotton seed, cucumbers, fig, flax, guava, lettuce leaf, maize, melons, okra, mustard greens, onions, bulb, green onion, mango, papaya, potato, sorghum, sugar apple and watercress. Other data on use pattern, methods of residue analysis, residue in food in commerce or at consumption and national residue limits were provided by the Governments of Australia, The Netherlands, Poland, Thailand and the UK.

IDENTITY

ISO common name: malathion

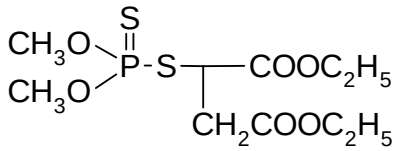
Chemical names:

IUPAC: diethyl (dimethoxythiophosphorylthio)succinate
S-(1,2-bis(ethoxycarbonyl)ethyl *O,O*-dimethyl phosphorodithioate

CA: diethyl [(dimethoxyphosphinothioyl)thio]butanedioate

CAS number: 121-75-5

Structural formula:



Molecular formula: $C_{10}H_{19}O_6PS_2$

Molecular weight: 330.3

Physical and chemical properties

Pure active ingredient:

Appearance: colourless to pale yellow liquid.

Vapour pressure: 5.3 mPa at 30°C

Melting point: 2.85°C

Octanol-water partition coefficient: K_{ow} = 560; log K_{ow} = 2.75

Solubility:	in water 148.2 mg/l at 25°C. readily soluble in hydrocarbons, esters and alcohols. moderately soluble in aliphatic hydrocarbons (62 g/l in n-hexane).	
Specific gravity:	1.23 g/ml at 25°C.	
Hydrolysis:	half-lives	107 days at pH 5 6.21 days at pH 7 0.49 days at pH 9
Photolysis:	half-life	156 days at pH 4, 25°C
Thermal stability:	stable at ambient temperatures (below 25°C). decomposes rapidly at temperatures above 100°C	

Technical material:

Min. purity: 95%.

Main impurities: *O*,*O*,*S*-trimethyl phosphorothioate.

Melting range: not relevant.

Stability: stable for at least two years when stored at ambient temperatures in the unopened original container.

Formulations

Table 1 shows the main types of formulation registered for use internationally. EC = emulsifable concentrate; ULV = ultra low volume.

Table 1. Formulations of malathion.

Product Formulation	Active ingredient	Concentration
CLEAN CROP Malathion 57 EC	Malathion	570 g/l
Fyfanon ULV	Malathion	1186 g/l
CLEAN CROP Malathion 8 Aquamul	Malathion	950 g/l
Fyfanon EC	Malathion	560 g/l
Fyfanon	Malathion	599 g/l
Fyfanon 8 LB. EMULSION	Malathion	958 g/l
Malathion 5	Malathion	599 g/l
Malathion 55	Malathion	599 g/l
CLEAN CROP Malathion 8 EC	Malathion	958 g/l
CLEAN CROP Malathion Methoxychlor Spray	Malathion Methoxychlor	240 g/l 240 g/l
Malathion ULV	Malathion	1186 g/l
CLEAN CROP Malathion ULV	Malathion	1162 g/l
CLEAN CROP Malathion ULV	Malathion	1173 g/l

Product Formulation	Active ingredient	Concentration
MARMAN Malathion ULV	Malathion	1173 g/l
MURPHY Liquid Malathion	Malathion	500 g/l

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Studies were submitted on the metabolism of radiolabelled malathion in laying hens and goats.

Hens. The metabolism, excretion and tissue distribution of [^{14}C]malathion (9.4 μCi/mg specific activity, 96.4% purity, labelled at the 2 and 3 positions of the succinate moiety) was studied in the hen (Cannon *et al*., 1993). Four laying hens were dosed daily for 4 days with encapsulated malathion and corn starch. Each dose corresponds to 3.8 mg malathion per hen (body weight about 1500 g) or 25 ppm in the feed based on an estimated feed intake of 150 g/hen. Four control hens received capsules containing corn starch only. Eggs were collected each day and the eight chickens were killed approximately 24 hours after administration of the last dose and heart, liver, muscle (light and dark meat), kidneys, skin plus underlying fat, other fat and the intestinal tract were collected, cubed and frozen until analysis.

The total radioactive residue (TRR) was determined in aliquots of the tissues, eggs, and excreta by scintillation counting after combustion to $^{14}CO_2$ or dilution with cocktail. The analytical methods employed for isolation of the radioactive residues included sequential extraction of tissue and egg samples with diethyl ether and methanol, both containing 0.1% trifluoracetic acid, followed by hydrolysis with sodium hydroxide, and enzymatic treatment with protease. The extracts were analysed by HPLC with a radio detector on reverse and anion exchange columns, with a carbohydrate column for the identification of glycerol.

Malathion was metabolized within 24 hours, with approximately 26% of the radioactivity excreted. The highest concentration of radioactivity was found in the faeces, with a TRR of 14 mg/kg malathion equivalents at day 2 and 7.65 mg/kg at day 7.

In the egg yolks collected on the first two days of treatment the TRR was ≤ 0.01 mg/kg, and increased to 0.96 mg/kg by the fourth day. Egg whites, however, contained significant radioactivity on day 1 and day 4 (Table 2).

Table 2. Total radioactive residues in egg yolks and whites.

Sample	^{14}C, mg/kg as malathion			
	Day 1	Day 2	Day 3	Day 4
Egg yolk	<0.01	0.03	0.35	0.96
Egg white	0.32	0.18	0.21	0.33

The results of serial solvent extraction showed that ethyl ether extracted most of the TRR on day 1 from egg white but subsequently the majority was extracted at the methanol and hydrolysis stages. By contrast ether extracted more from later samples of egg yolk (Table 3).

Table 3. Distribution of radioactive residues in extracts of egg whites and yolks.

Fraction	Egg white, % of TRR		Egg yolk, % of TRR	
	Day 1	Day 4	Day 2	Day 4
Ether/TFA	62.5	6.1	33.3	77.1
Methanol/TFA	9.4	21.2	-	7.3
0.2N NH_4OH	3.1	3.0	-	-
3N NaOH	3.1	48.5	66.7	26.0
Total extracted	78.1	78.8	100.0	110.4

The highest concentration of radioactivity in tissue was observed in kidney and liver samples (1.08 and 0.77 mg/kg as malathion respectively), and the lowest level (0.11 mg/kg) was found in light and dark muscle (Table 4).

Table 4. Total radioactive residues in hen tissues.

Tissue	TRR, mg/kg as malathion
Liver	0.77
Kidney	1.08
Heart	0.28
Muscle	0.11
Fat	0.18
Skin	0.16
GIT	0.42

The extraction of the tissues showed a fairly broad distribution of activity between ether, methanol and alkaline hydrolysis fractions, except in fat where the activity was mainly in the ether fraction (Table 5).

Table 5. Distribution of radioactive residues in extracts of tissues.

Fraction	Liver, % of TRR	Muscle, % of TRR	Fat, % of TRR
Ether/TFA	29.7	27.3	100.0
Methanol/TFA	21.6	18.2	5.6
0.2N NH_4OH	1.4	-	-
3N NaOH	23.0	63.6	5.6
Total extracted	75.7	109.1	111.2

Malathion was found to be used as a carbon source, with the radioactivity being incorporated in fatty acids, glycerol, tricarboxylic cycle acid intermediates and protein (Table 6). These components contained ^{14}C at levels from 0.01 to 0.2 mg/kg malathion equivalent. No malathion or any products of immediate metabolism were observed at levels exceeding 0.02 mg/kg in any of the samples, except the white from one egg on day 1, in which significant activity as malathion carboxylic acid was detected. This result, however, was attributed to contamination by the faeces, extracts of which were shown to contain the metabolite.

Table 6. Identification of radioactive residues in fat and tissues of laying hens.

Sample	^{14}C, % of TRR						
	Triglyceride	Oleic acid	Pyruvic acid	Lactic acid	Fumaric acid	Protein	Total
Heart	-	-	-	3.6	-	28.6	32.2
Kidney	4.6	-	1.5	2.3	-	26.0	34.4
Liver	32.4	18.9	12.2	-	1.4	29.7	94.6
Muscle	-	-	-	18.2	-	36.4	54.6
Fat	66.7	-	-	-	-	22.2	88.9
Skin	37.5	-	-	-	-	50.0	87.5
Egg white (day 2)	-	-	-	-	-	61.1	61.1
Egg yolk (day 3)	65.7	-	-	-	-	28.6	94.3

Goats. The metabolism, excretion, and [^{14}C]malathion (9.8 μCi/mg specific activity, 96.4% purity, labelled at the 2 and 3 positions of the succinate moiety) were studied in the goat (Cannon *et al.*, 1992). Two animals were dosed with 172.2 mg malathion in capsule per goat per day for five days, 115 ppm in the diet based on an estimated feed intake of 2 kg/goat/day. The test animals and the control were slaughtered approximately 24 hours after the last dose. Urine, faeces, and milk were collected during the dosing period, and heart, liver, muscle, fat and rumen contents were analysed. The samples were homogenised, and aliquots were either combusted to $^{14}CO_2$ or directly counted to determine the TRR. The analytical procedures were similar to those for hens. Milk was fractionated into fat, whey and casein components, which were analysed by HPLC in reverse mode and with columns designed for carbohydrate separation.

Malathion was rapidly metabolized after dosing, with 45-70% of the radioactivity excreted within 24 hours (Table 7).

Table 7**.** Excretion of radioactive residues by goats.

Day	^{14}C, % of dose			
	Goat 1		Goat 2	
	Urine	Faeces	Urine	Faeces
1	60.3	9.3	41.9	4.5
2	28.8	13.8	64.0	8.2
3	56.9	13.8	68.8	8.6
4	43.9	16.9	64.0	9.1
5	56.3	14.6	63.2	9 7
Average	49.2	13.7	60.4	8.0

Most of the ^{14}C residues in milk were extracted by polar solvents (Table 8) and up to 93% of the residues were identified (Table 9). Radioactivity in milk increased from 1.4 mg/kg as malathion at day 1 to 2.5 mg/kg at day 4 and decreased to 2.14 mg/kg at day 5.

Table 8. Distribution of radioactive residues in extracts of milk (average values**).**

Fraction	Day 1, % of TRR	Day 5, % of TRR
Hexane	5.7	5.6
Ether	15.2	13.8
Methanol/TFA	74.4	68.5
0.2N NH_4OH	4.9	4.2

Fraction	Day 1, % of TRR	Day 5, % of TRR
3N NaOH	0.4	0.6
Total extracted	100.6	92.7

Table 9**.** Identification of radioactive residues in milk.

	^{14}C, % of TRR			
	Triglycerides	Lactose	Protein	Total
Goat 1	16.8	70.5	6.0	93.3
Goat 2	19.5	58.6	4.1	82.2

The mean TRR in tissues was 2.26 mg/kg as malathion in liver, 1.96 mg/kg in kidneys, 0.38 mg/kg in heart, 0.24-0.28 mg/kg in muscle, 1.0 mg/kg in fat (omental) and 1.88 mg/kg in rumen contents. The radioactivity extracted by polar and non-polar solvents and after hydrolytic action was more evenly distributed in liver and heart extracts than in fat (Table 10)

Table 10. Distribution of radioactive residues in extracts of fat and tissues.

Fraction	Fat, % of TRR	Liver, % of TRR	Heart , % of TRR
Ether/TFA	83.8	18.0	21.1
MeOH/TFA	3.7	40.9	29.0
0.2N NH_4OH	2.0	4.5	2.7
3N NaOH	3.0	30.2	50.2
Total extracted	92.5	93.6	103.0

Malathion was utilized as a carbon source for the production of triglycerides, acids of the tricarboxylic acid cycle and lactose. In summary, 82-93% of the TRR in milk samples, 70-80% in fat, 94-115% in muscle, and 77-83% in other tissues was identified. The distribution of the identified products in fat and tissues is shown in Table 11.

Table 11. Identification of radioactive residues in fat and tissues of goats.

Sample	^{14}C, % of TRR							
	Tri-glyceride	Oleic acid	Stearic acid	Pyruvic acid	Lactic acid	Fumaric acid	Protein	Total
Fat								
- back	71.8	6.3	-	-	-	-	2.3	80.4
- omental	68.0	2.0	-	-	-	-	4.7	74.7
-perirenal	61.3	-	2.8	-	-	-	5.6	69.7
Heart	12.8	-	-	5.1	10.3	2.6	46.2	77.0
Kidney	5.8	1.8	-	8.2	9.4	2.3	46.2	73.8
Liver	3.1	4.5	1.3	27.8	5.8	1.8	39.0	83.3
Muscle								
- Semi-m	53.8	-	-	11.5	11.5	-	38.5	115.3
- L. Dorsi	50.0	8.3	-	-	11.1	2.8	22.2	94.4

In kidney, the metabolites malathion monocarboxylic acid and dicarboxylic acid were detected at 0.06 mg/kg and <0.05 mg/kg as malathion respectively. These were found in high concentration in the urine. No malathion or any products arising from primary metabolism were

observed at levels above 0.05 mg/kg in any other sample analysed. Proposed metabolic pathways of malathion in goats are shown on Figure 1. Structures of standards used in the metabolism studies on animals and plants are shown in Figure 2.

Plant metabolism

The metabolism of [^{14}C]malathion in cotton plants was examined by Wootton and Johnson (1992a). The plants were grown outdoors in pots in California. [^{14}C]malathion (7.4 mCi/mol specific activity, 97.4% purity, labelled at the 2 and 3 positions of the succinate moiety) was sprayed on the field at a rate of 1.46 kg ai/ha at 9 to 33 day intervals, with a total of ten applications. Cotton leaves and mature and immature bolls were separately collected approximately 18 hours after the last application. Mature cotton bolls were manually processed into seed, lint and gin trash. The TRR in the immature bolls, lint and gin trash was 55.6, 217 and 428 mg/kg malathion equivalents respectively. The radioactive residues were isolated by successive extraction of the samples with acidified acetonitrile/water, methanol/chloroform/acetone and potassium phosphate buffer, this last extract being partitioned with chloroform. The organic extracts were analysed by HPLC and TLC. The distribution of the radioactive residues in the various extracts of cotton leaves and seed is shown in Table 12.

Table 12**.** Distribution of radioactive residues in extracts of cotton leaves and seed.

Extract	Leaves, % of TRR	Seed, % of TRR
Hexane	—	26.9
Chloroform	49.9	12.2
Aqueous	16.1	5.0
Buffer	15.5	7.9
Extracted solids	15.4	15.3
Recovered	96.9	67.3

Figure 1. Proposed metabolic and incorporation scheme of malathion in lactating goats.

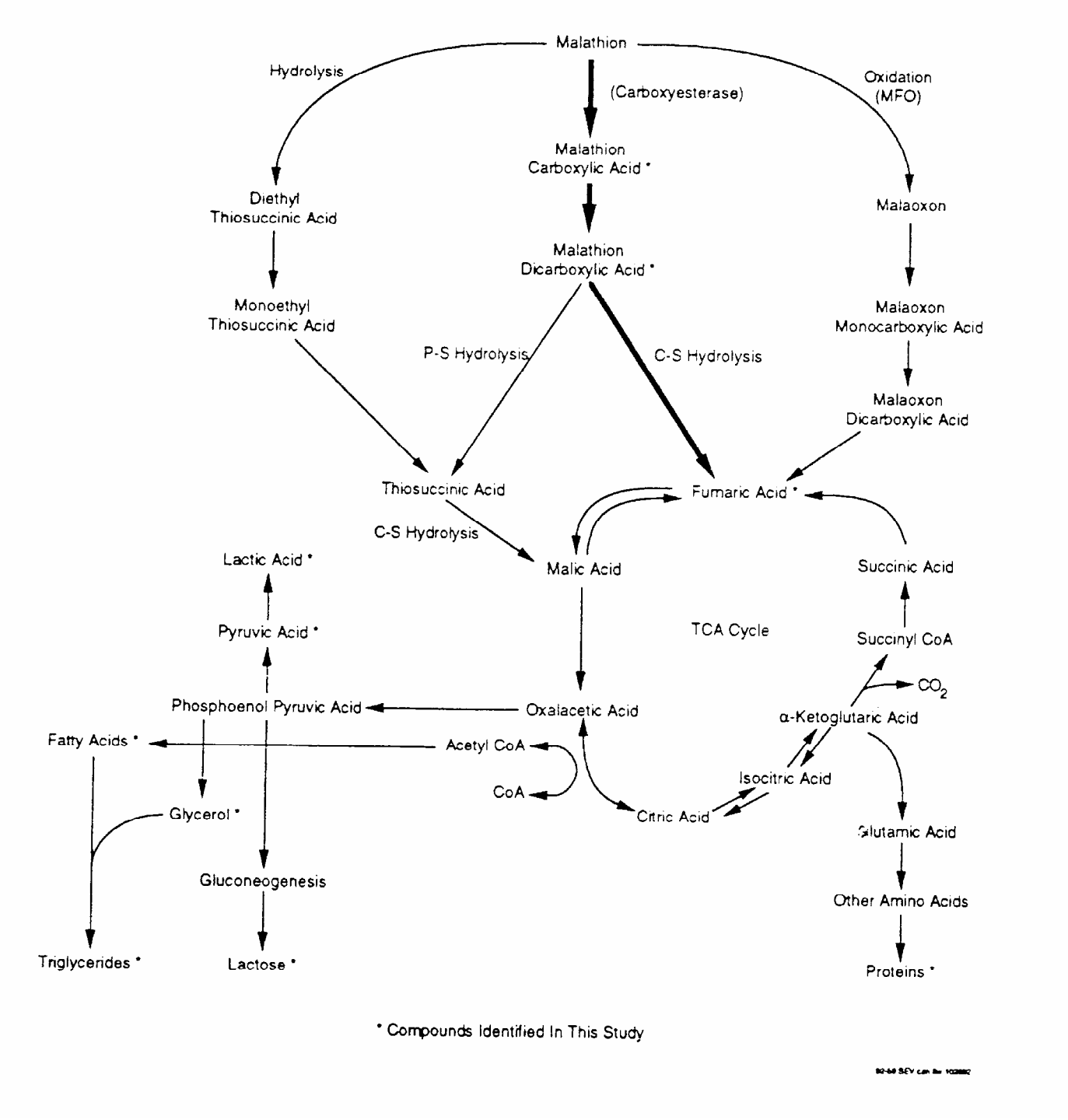
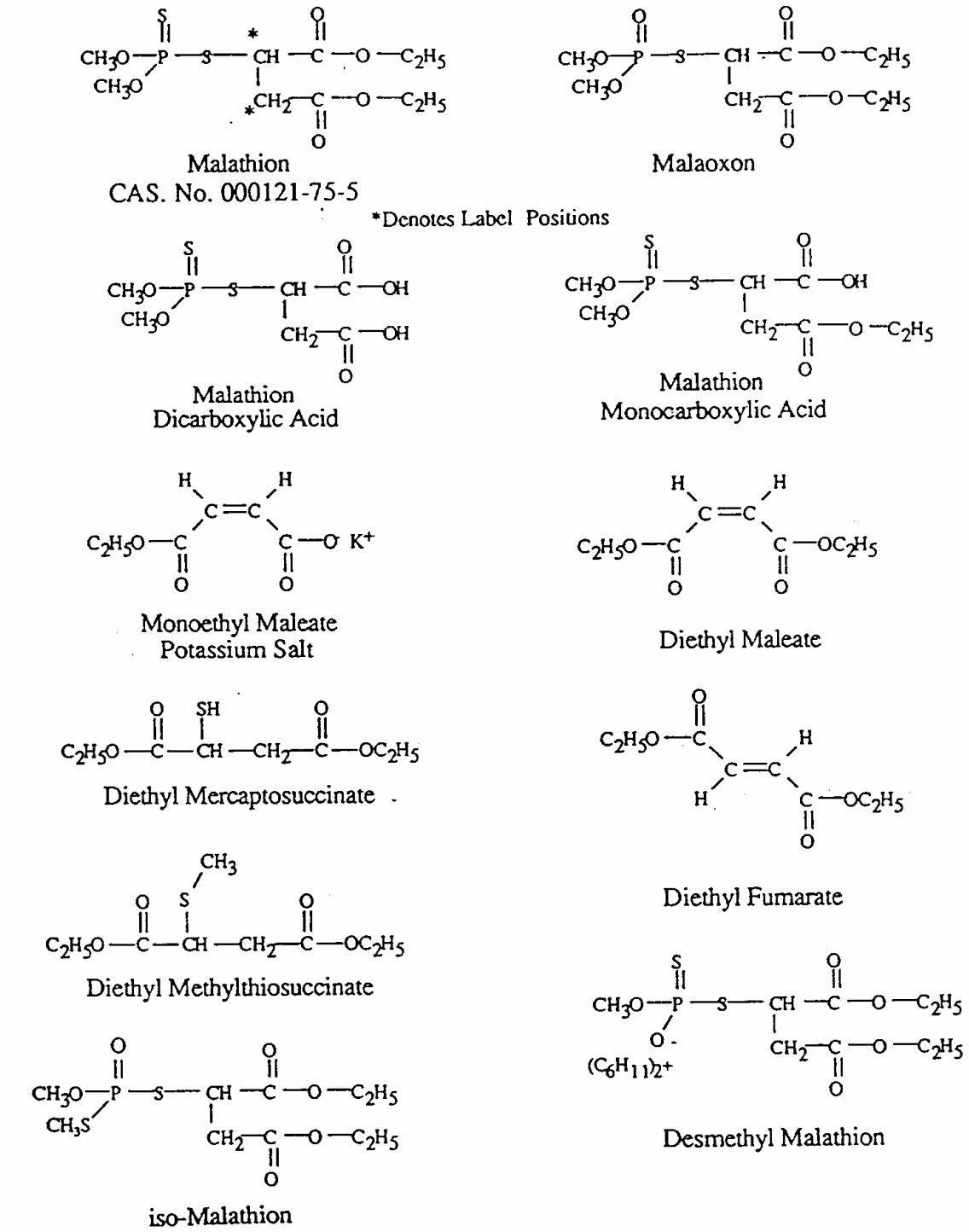


Figure 2. Structures of malathion and metabolite standards used in the metabolism studies.



Malathion was the major component identified in organic solvent extracts of the cotton seed and malathion monocarboxylic acid the most prominent metabolite. Other compounds identified are shown in Table 13. In the polar extract succinate was the major component (2.0% of the TRR), others being citrate and fumarate. Radioactivity was also found to be incorporated into starch, protein, pectin, lignin, hemicellulose and cellulose (total 14.6% of the TRR).

Table 13. Identification of radioactive residues in cotton seed.

Compound	% of TRR	mg/kg as malathion
Malathion	32.5	48.70
Malaoxon	0.2	0.3
Diethyl maleate	0.2	0.3
Monoethyl maleate	0.2	0.3
Malathion dicarboxylic acid	<0.1	<0.01
Malathion monocarboxylic acid	2.6	3.9
Diethyl fumarate	0.3	0.45
Diethyl methylthiosuccinate	<0.1	<0.01
Desmethyl malathion	0.1	0.15
Malathion mixed ester (methyl + ethyl)[1]	0.5	0.75
Tetraethyl dithiodisuccinate	0.3	0.45
TOTAL	36.7	55.3

[1]This residue was found to be an impurity in malathion, so the malathion residue was 33% (49.45 mg/kg).

Wheat. The metabolism of [^{14}C]malathion (7.16 mCi/mol specific activity, 97% purity, labelled at the 2 and 3 positions of the succinate moiety) in wheat forage, grain and straw was examined in a study conducted in California (Wootton and Johnson, 1992b). The compound was applied three times at 1.68-1.8 kg ai/ha when plants were at the late tillering stage, the boot stage and approximately 1 week before the final harvest. Forage samples were collected one week after the second treatment. Mature wheat was separated into straw, grain and chaff. The radioactive residues were isolated as before. The organic extracts were analysed by HPLC and TLC. The distribution of radioactive residues in various extracts is summarized in Table 14.

Table 14. Distribution of radioactive residues in extracts of wheat forage, grain and straw.

Extract	Forage, % of TRR	Grain (%TRR)	Straw, % of TRR
Chloroform	32.7	35.0	21.3
Aqueous	22.5	5.5	39.2
Buffer	16.2	12.8	6.3
Extracted solids	17.4	28.9	17.2
Recovered	88.8	82.2	84.0

Malathion was the major component identified in organic solvent extracts of the wheat fractions, and malathion monocarboxylic and dicarboxylic acids the major metabolites (Table 15). ^{14}C residues were also found to be incorporated in starch, protein, pectin, lignin, hemicellulose and cellulose.

Table 15. Identification of radioactive residues in wheat forage, grain and straw.

Compound	Forage		Grain		Straw	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
Malathion	7.0	3.76	26.6	2.76	10.4	13.94
Malaoxon	ND	ND	0.4	0.04	0.1	0.2
Diethyl maleate	0.6	0.32	ND	ND	0.4	0.5
Monoethyl maleate	ND	ND	0.2	0.02	ND	ND
Diethyl mercaptosuccinate	ND	ND	ND	ND	<0.1	0.03
Malathion dicarboxylic acid	4.9	2.63	1.1	0.11	0.1	0.09
Malathion monocarboxylic acid	6.0	3.22	0.5	0.05	7.3	9.8
Diethyl fumarate	0.2	0.11	ND	ND	0.1	0.22
Diethyl methylthiosuccinate	0.1	0.05	<0.1	<0.01	ND	ND
Desmethyl malathion	0.4	0.21	ND	ND	0.1	0.11
Malathion mixed (methyl + ethyl) ester[1]	8.1	4.35	0.8	0.08	0.6	0.79
Tetraethyl dithiodisuccinate	0.3	0.16	ND	ND	0.1	0.13
TOTAL	27.6	14.81	29.6	3.06	19.3	25.81

ND = not detected (<0.01 mg/kg)
[1]This residue was found to be an impurity in malathion, so the total malathion residue is 8.11 mg/kg in forage, 2.84 mg/kg in grain, and 14.73 mg/kg in straw.

Alfalfa. The metabolism of [^{14}C]malathion (2.84 mCi/mmol specific activity, 97% purity, labelled at the 2 and 3 positions of the succinate moiety) in alfalfa forage and hay was examined in a study conducted in California (Wootton and Johnson, 1992c). Malathion was applied at 2.0-2.1 kg ai/ha, when plants were 6-12 and 18-24 inches respectively. Mature plants (55 days post planting) were harvested 18 hours after the last application. After extraction with acidified organic solvents, the labelled residues were identified by HPLC and TLC. The distribution of the radioactive residues in the extracts is shown in Table 16.

Table 16. Distribution of radioactive residues of malathion in extracts of alfalfa forage and hay.

Fraction	Forage, % of TRR	Hay, % of TRR
Chloroform	57.2	27.5
Aqueous	15.9	17.7
Buffer	9.0	19.6
Extracted solids	3.9	16.6
Recovered	86.0	81.4

The major component was malathion, and the most prominent metabolite was malathion monocarboxylic acid (Table 17). ^{14}C residues were also found to be incorporated in starch, protein, pectin, lignin, hemicellulose and cellulose.

Table 17. Identification of residues in organic extracts of alfalfa forage and hay.

Compound	Forage		Hay	
	% of TRR	mg/kg	% of TRR	mg/kg
Malathion	40.5	56.72	14.6	31.33
Malaoxon	ND	ND	0.8	1.82
Iso-malathion	ND	ND	0.2	0.43
Diethyl maleate	0.5	0.74	0.2	0.47
Monoethyl maleate	ND	ND	0.3	0.69
Diethyl mercaptosuccinate	0.2	0.23	0.1	0.16
Malathion dicarboxylic acid	ND	ND	1.5	3.42
Malathion monocarboxylic acid	9.8	13.77	2.7	5.79
Diethyl methylthiosuccinate	0.1	0.17	ND	ND
Diethyl fumarate	0.1	0.21	0.1	0.38
Desmethyl malathion	0.5	0.67	0.2	0.52
Malathion mixed (methyl + ethyl) ester[1]	1.5	2.08	1.8	3.81
Tetraethyl dithiodisuccinate	<0.1	0.04	0.6	1.26
TOTAL	53.2	74.63	23.1	50.09

ND = not detected (<0.01 mg/kg
[1] This residue was found to be an impurity in malathion, so the total malathion residue is 35.14 mg/kg in hay and 58.80 mg/kg in forage.

Lettuce. The metabolism of [^{14}C]malathion (2.3 mCi/mmol specific activity, 98.8% purity, labelled at the 2 and 3 positions of the succinate moiety) in lettuce was examined in a study conducted in California (Wootton and Johnson, 1992d). Malathion was applied 6 times at a rate of 2.0 kg ai/ha and plants were harvested 14 days after the last treatment. After sample extraction with acidified organic solvents, the labelled compounds were identified by TLC and HPLC. The major component identified in organic solvent extracts of treated lettuce was malathion, representing 36.8% of the TRR (160.9 mg/kg). The most prominent metabolite was malathion monocarboxylic acid at 12.8% of the TRR (56 mg/kg as malathion). Malaoxon was present at 1.2% of the TRR (5.3 mg/kg). Other compounds identified are shown in Table 18. Polar extracts contained citrate, succinate and fumarate.

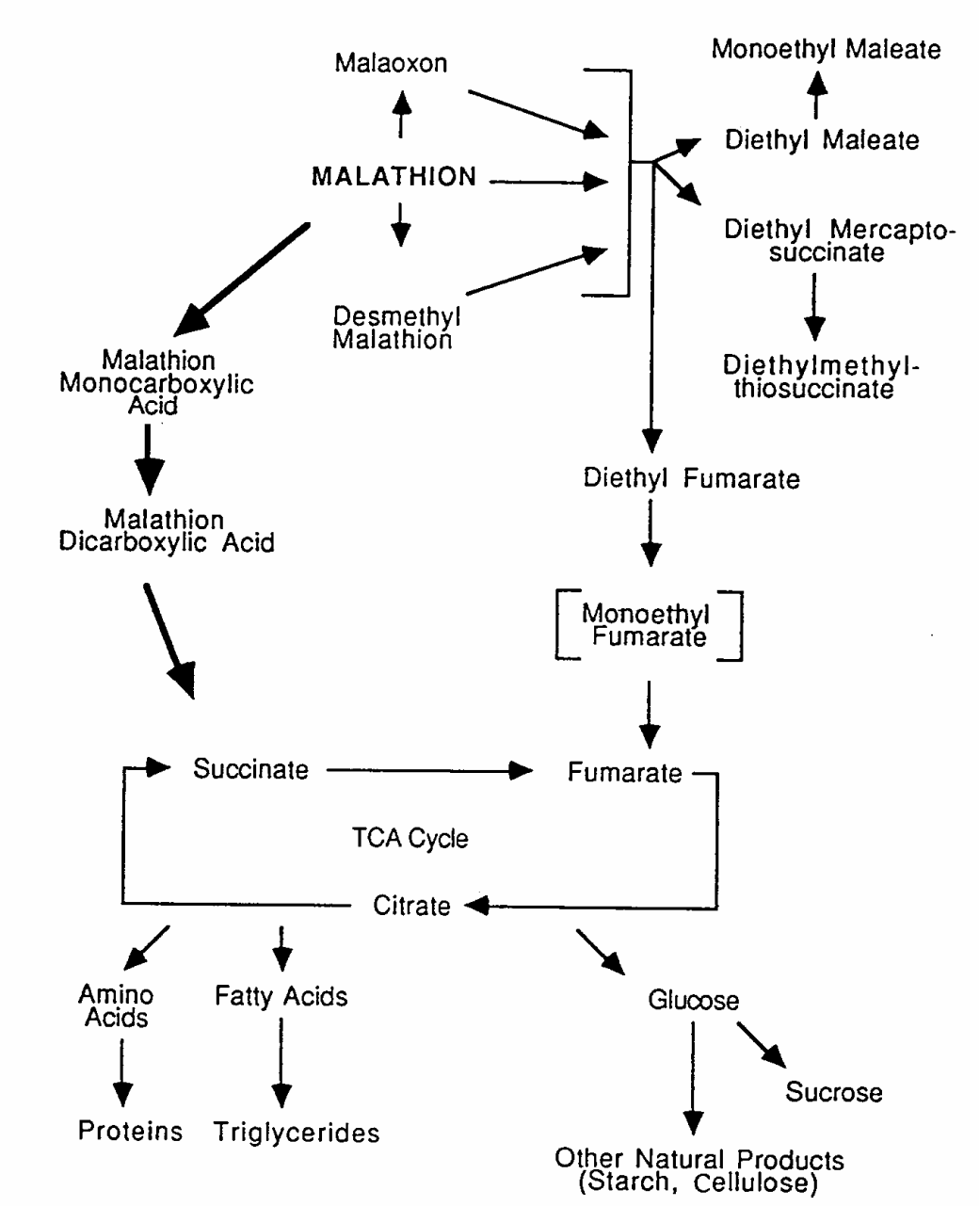
Table 18. Identification of radioactive residues in lettuce.

Component	% of TRR	mg/kg
Malathion	30.9	135.07
Malaoxon	1.2	5.25
Diethyl maleate	0.4	1.74
Monoethyl maleate	0.3	1.38
Malathion dicarboxylic acid	0.9	3.93
Malathion monocarboxylic acid	12.8	56.12
Diethyl fumarate	0.1	0.44
Desmethyl malathion	0.3	1.31
Malathion mixed (methyl + ethyl) ester [1]	5.9	25.79
Tetraethyl dithiodisuccinate	0.2	0.88

[1] This residue was found to be an impurity in malathion, so the total malathion residue in lettuce was 36.8% (160.86 mg/kg)

The metabolism of malathion is similar in alfalfa, lettuce, wheat and cotton and proceeds via de-esterification to the dicarboxylic acid which is cleaved to give succinic acid which is incorporated into the plant constituents (Figure 3). Analysis of polar extracts showed that ^{14}C activity was associated with citrate, succinate and fumarate moieties. The ^{14}C-residues in the alfalfa and wheat forage and hay, wheat grain and straw and cotton seed extracted solids were associated with endogenous plant constituents such as starch, protein, lignin and cellulose.

Figure 3. Proposed metabolic pathways of malathion in wheat, alfalfa, cotton and lettuce.



Environmental fate in soil

The adsorption and desorption of malathion (90 μCi/mg specific activity, 96% purity, labelled at the 2 and 3 positions of the succinate moiety) were studied in 5 soils using the batch technique according to US-EPA (FIFRA) guideline N163-1 and complying with GLP (Blumhorst, 1989). Initial concentrations were approximately 100, 10, 1 and 0.1 μg/ml and the solution:soil ratio was 5:1. Treated samples were flushed with nitrogen, and the tubes capped and shaken for 2 hours at 22°C. For desorption, 10 ml 0.01 M $CaCl_2$ was added to the soil suspension remaining in the tubes and the tubes shaken and centrifuged as before. Regression analysis of the log transformed data showed that the adsorption and desorption isotherms were highly linear over the concentration ranges and well described in Freundlich equation. The K_d and K_{oc} constants, together with the soil properties are shown in Table 19.

Table 19. Soil properties and malathion adsorption and desorption constants.

Soil	pH	CEC[1] meq/100g	Clay content	Organic matter %	Organic carbon %	Adsorption		Desorption	
						K_d	K_{oc}	K_d	K_{oc}
Sandy loam	6.9	5.6	8	1.1	0.55	0.83	151	0.89	161
Sand	6.2	1.9	4	0.8	0.4	1.23	308	1.67	418
Loam	6.1	10.6	18	2.0	1.0	1.76	176	1.63	163
Silt loam	7.4	15.7	26	2.7	1.35	2.47	183	2.08	154
Sandy loam	4.5	5.6	10	1.2	0.6	1.60	267	2.03	338

[1] cation exchange capacity

Malathion was adsorbed in moderate amounts by the soils examined, which places it in the medium mobility class. Adsorption generally increased as soil organic matter, clay content and cation exchange capacity increased.

Malathion was fairly stable under the experimental conditions, accounting for 74.2 to 98.6% of the TRR in the adsorption and desorption solutions. The ß-monocarboxylic acid was the main degradation product detected, ranging from 0.1% of the TRR in sand to 19% in loam (Table 20).

Table 20. Formation of malathion carboxylic acid in soil solution systems.

Soil	Adsorption solution, % of TRR		Desorption solution, % of TRR	
	Malathion	β-monocarboxylic acid	Malathion	β-monocarboxylic acid
Sandy loam	92.8	3.3	93.5	5.3
Sand	98.6	0.1	96.4	0.3
Loam	88.7	6.8	74.2	19
Silty loam	87.8	8.6	83.4	13.4
Sandy loam	94.3	1.4	94.3	2.2

The aerobic degradation of malathion was evaluated in a study with a loam soil representative of agricultural soils in the Midwest of the USA (Blumhorst, 1990). [^{14}C]malathion was applied to a nonsterile soil (2 samples) and sterile soil (1 sample) at a rate of 6.88 - 8.86 mg/kg dry weight (7.63 - 7.75μCi), corresponding to the maximum label rate of 7.01 kg ai/ha. Samples were kept in the dark at 22°C. Sub-samples for analysis were taken immediately after treatment, after 6 hours and after 1, 2, 3, 4, 7, 14 and 92 days. In the non-sterile soil, malathion was rapidly degraded with an average half-life of 4.9 hours. After 6 hours malathion represented, on average, 21.9% of the applied ^{14}C which dropped to 2.6% after 1 day. The main extractable product was malathion dicarboxylic acid, representing a mean of 13.8 and 1.1% of the TRR after 6 hours and 4 days respectively. Bound residues mainly associated with the humin fraction of soil organic matter, and $^{14}CO_2$ were both

significant products (>50% of the TRR at day 7). Dissipation of ^{14}C by volatilization was insignificant.

The degradation of [^{14}C]malathion under aerobic and anaerobic conditions on a loamy sand soil collected in Buelah, Arkansas was studied by Saxena (1988). Samples were fortified with [^{14}C]malathion at 3.12 mg/kg and maintained at 25°C in the dark. Humidified air was drawn through the system to maintain aerobic conditions and duplicate samples were taken after 8, 16 and 26 hours and 3, 7, 11, 21, 31, 63, 94 and 162 days. After 26 hours, 4 samples were rendered anaerobic by flooding with water and nitrogen until the end of the study and sub-samples were taken 30 and 62 days after flooding.

Malathion was degraded with a half-life of 1 day under aerobic conditions. The major degradation products were $^{14}CO_2$ (up to 58.4% of the TRR on day 162), soil bound residues (up to 25.7% of the TRR on day 94) and malathion dicarboxylic acid (up to 62.3% of the TRR on day 7). Under anaerobic conditions the half-life of malathion was less than 30 days, although the exact value could not be determined with only 2 samples. The major degradation products were the same as for aerobic degradation.

The dissipation of malathion after application to bare soil and cotton was evaluated in a field dissipation study conducted in California (Rice *et al.*, 1990; Jacobsen *et al.*, 1993). Six applications at a rate of 1.13 kg ai/ha were made at 7-day intervals. Soil core samples were taken after each application and 1, 3, 7, 14 and 28 days after the final application. The results are shown in Table 21.

Table 21. Malathion residues (mg/kg dry weight) in soil samples taken from a treated crop plot and bare ground plot after each application and one day after the last application (LOD = 0.01 mg/kg).

	Crop plot							Bare ground plot						
Soil depth	1st appln	2nd appln	3rd appln	4th appln	5th appln	6th appln	+1 day	1st appln	2nd appln	3rd appln	4th appln	5th appln	6th appln	+1 day
0-15 cm	0.055	0.072	0.13	0.11	0.13	0.082	0.14	0.088	0.037	0.087	0.047	0.062	0.067	0.11
15-30 cm	0.064	0.047	0.14	0.072	0.072	0.066	0.13	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD
30-45 cm	<LOD	<LOD	0.023	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD	<LOD

Residues of malathion could not be detected in any soil samples later than one day following the last application. Malathion dicarboxylic acid was only detected at 0.11 mg/kg in soil from the bare ground plot 1 day after the final application and in one sample from the 30-45 cm soil layer in the cotton plot after the second application (0.016 mg/kg). Residues of malaoxon could not be detected in any sample analysed.

The dissipation half-life of malathion could not be determined because the residues dissipated too rapidly.

The photodegradation of [^{14}C]malathion (10 mg/kg) on the surface of sandy loam soil was studied under a 12 hours light/12 hours dark cycle and a dark control over a 30-day period (Dykes *et al.*, 1990). The soil was maintained at about 25°C and samples were taken after 1, 4, 7, 11, 21, 26 and 30 days. The rate constant and extrapolated half-life of malathion were 0.00399 day^{-1} and 173 days respectively in the exposed soil and 0.01092 day^{-1} and 63.5 days respectively in the control soil. The shorter half-life in the control sample is believed to be a result of increased microbial activity on the test compound. After 30 days, the total volatiles accounted for <6% of the initial dose in both exposed and unexposed systems, and malathion accounted for 83.2 and 93.4% of the recovered activity in the exposed and control soils respectively.

The leaching potential of [^{14}C]malathion and its degradation products was evaluated in a study on four types of soil (Nixon, 1995). Flasks containing treated soil (5.3 mg/kg of malathion, 75% field capacity) were incubated in the dark at 25°C and sampled at 0 and 21 hours (sand), 0, 2 and 4

hours (sandy loam) and 1.5 hours (loam and silty clay). Once half-lives were determined (Table 22), six flasks of each soil were treated and aged for approximately one half-life. Two flasks of each soil were sampled following dosing, two at the ageing period and two were mixed thoroughly and added to the top of replicate columns containing untreated soil of the same type. Malathion and/or its degradation products exhibited moderate mobility with 5 to 74.4% of the applied radiocarbon passing through the columns in the leachate (Table 22).

Table 22. ^{14}C distribution in leachate and soil sections following column leaching of aged residues under saturated flow conditions.

Soil	Half-life, hours	Total leachate, % of applied ^{14}C	Soil sections, cm
Sand	14.3	48.4	50.9
Sandy loam	2.1	74.4	20.2
Loam	0.5	61.8	29.8
Silty clay	0.9	5.0	99.1

[^{14}C]malathion was present only in sand leachate at 1.9% of the applied radioactivity. Dicarboxylic and monocarboxylic acids were present in all soils except silty clay, the dicarboxylic acid being the main product (Table 23). The mono- and dicarboxylic acids showed greater potential for leaching, but this was mitigated by their relatively rapid mineralization.

Table 23. Quantitative characterization of ^{14}C malathion residues in the leachate fractions (% of applied radioactivity).

Soil	Fraction	Malathion	Dicarboxylic acid	Monocarboxylic acid
Sand	2nd	1.9	17.5	13.3
Sandy loam	1st	nd	6.9	0.8
	2nd	nd	47.6	4.2
	3rd	nd	11.8	0.1
	4th	nd	2.8	nd
Loam	1st	nd	10	6.6
	2nd	nd	20.4	6.4
	3rd	nd	12.4	1.2

The volatility of malathion from a silt loam soil was assessed in a study using [^{14}C]malathion formulations at the recommended field rate with air flows of 100 or 300 ml/min and soil at 50% or 75% field capacity (Spare *et al.*, 1991). The results showed little or no recovery of volatiles either as malathion or CO_2 with the exception of the EC formulation at 50% soil moisture and 100 ml/min gas flow, where 26.5% of the applied dose was recovered as CO_2. There was no discernible pattern of volatility with soil moisture or purge flow rate (Table 24).

Table 24. Volatility of malathion in three formulations.

Formulation	Maximum air concentrations, µg malathion/m^3	Maximum volatility, µg malathion/cm^2/h
RTU[1]	5.4 - 21.5	1.2-3.6 x 10^{-3}
ULV[2]	1.8 - 5.4	0.4 x 10^{-3}
EC[3]	18.4 - 74.5	1.8 x 10^{-3} - 1.7 x 10^{-2}

[1]Ready-to-use
[2]Ultralow volume
[3]Emulsifiable concentrate

Environmental fate in water/sediment systems

The degradation of malathion in a water/sediment system was evaluated under aerobic and anaerobic conditions (Blumhorst, 1991a,b;1997). Samples were fortified with [^{14}C]malathion at 1.108 - 1.02 mg/kg and maintained at 22°C in the dark. In the aerobic study, sub-samples of water and sediment were taken for analysis immediately after treatment and after 6 hours and 1, 3, 7, 14 and 30 days. Under anaerobic conditions, sampling was continued to 118 days. The initial degradation products were monocarboxylic acids of malathion (α and β isomers), demethyl monocarboxylic acids, dicarboxylic acid and demethyl dicarboxylic acid (Table 25) which underwent further degradation.

Table 25. Half-life of malathion and maximum product concentrations in aerobic and anaerobic water/sediment systems.

	Aerobic		Anaerobic	
	water	sediment	water	sediment
Half-life (days)	1.09	2.55	2.49	2.45
Monocarboxylic acids, % of applied ^{14}C	28.81 (day 3)	3.61 (6 hours)	28.46 (day 4)	4.52 (6 hours)
Dicarboxylic acid, % of applied ^{14}C	46.38 (day 7)	6.39 (day 7)	20.91 (day 14)	5.20 (day 4)
Demethyl monocarboxylic acids, % of applied ^{14}C	23.87 (day 30)	4.69 (day 30)	20.77 (day 7)	8.06 (day 45)

Dissipation by volatilization was minimal in both studies (<0.5 and <0.1% of the applied ^{14}C, in aerobic and anaerobic conditions, respectively). Under anaerobic conditions, total radioactive residues in the sediment (extracted + bound) gradually decreased with time whereas mineralization increased, accounting for 56% of the applied radioactivity at day 118 after application. In the aerobic system, mineralisation and bound residue formation increased to 24 and 10% of the applied ^{14}C, 30 days after treatment respectively.

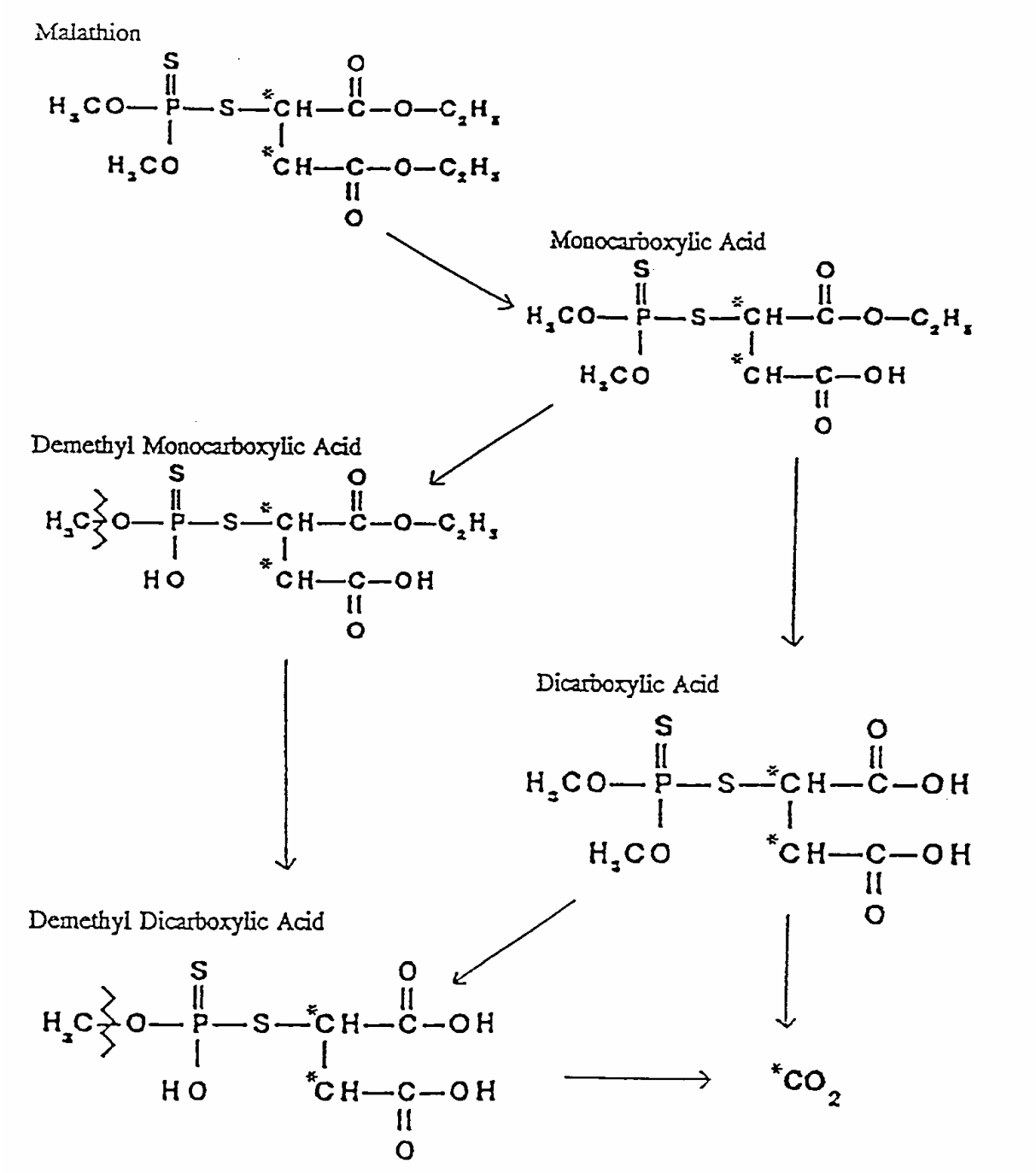
Proposed degradation pathways in aerobic aquatic system are shown in Figure 4.

METHODS OF RESIDUE ANALYSIS

Analytical methods for the determination of malathion and malaoxon in wheat grain and its processed commodities, cotton seed, alfalfa, head lettuce, green onions, oranges and their processed commodities, corn, tomatoes and their processed commodities and avocados were reported (Buttrey and Butz, 1995). Malathion and malaoxon are extracted from most samples with acetonitrile or acetonitrile/water (80:20). Dry samples are hydrated before the extraction. Lipids are removed from the extracts with hexane and the analytes are partitioned 3 times with dichloromethane. Clean-up of the organic extract is on activated carbon and silica gel solid-phase extraction cartridges. The analytes are quantified by gas chromatography with a flame photometric detector in the phosphorus mode (FPD-P). Recoveries of malathion and malaoxon averaged 89.6% and 98.2% respectively. The LOD is 0.01 mg/kg for all raw and processed human food and 0.05 mg/kg for raw and processed animal feed.

Multi-residue methods for the analysis of pesticides amenable to gas chromatography were reported by The Netherlands. Non-fatty samples (<5% fat content) are extracted with ethyl acetate and sodium sulfate or acetone followed by partition with dichloromethane and petroleum ether. No clean-up is necessary and the analytes are determined by GLC with a nitrogen-phosphorus detector (NPD) or ion trap detector. The LOD for malathion and malaoxon is 0.02 mg/kg and recoveries ranged from 97 to 106%.

Figure 4. Proposed malathion degradation pathway in aerobic aquatic system (*labelled position)



In market basket survey and monitoring programmes in Australia organophosphorus insecticides are extracted with acetone, partitioned into dichloromethane/hexane and cleaned up by gel permeation chromatography. The analytes are determined by GLC with an NPD or FPD-P with an

LOD of 0.01 or 0.02 mg/kg. In another method dialysis through a semi-permeable membrane and alumina column clean-up preceded analysis by GLC.

Stability of residues in stored analytical samples

Clayton (1996) assessed the stability of malathion and malaoxon in various raw agricultural and processed commodities during freezer storage for twelve months. Duplicate samples were fortified with 0.50 mg/kg malathion and malaoxon and stored at <-5°C up to 12 months. The results show that the analytes are stable under the conditions of the study, with 69 to 105% of malathion and 91 to 109% of malaoxon remaining (Tables 26 and 27).

Table 26. Storage stability of malathion and malaoxon in raw commodities at <-5°C.

Sample	Analyte	Mean % remaining after nominal storage periods (months)[1]					
		0	1	2	3	6	12
Cotton seed	Malathion	89	79	108	94	91	92
	Malaoxon	101	57	80	99	121	90
Wheat grain	Malathion	94	63	68	77	76	60
	Malaoxon	98	75	77	76	78	74
Wheat forage	Malathion	84	76	76	70	69	68
	Malaoxon	84	90	88	82	80	95
Wheat straw	Malathion	72	82	102	76	88	79
	Malaoxon	86	77	89	67	83	81
Leaf lettuce	Malathion	99	NA	99	97	103	94
	Malaoxon	97	NA	117	99	111	109
Potato tubers	Malathion	88	75	83	88	100	66
	Malaoxon	92	87	93	90	91	70
Tomato fruit	Malathion	83	90	96	109	100	91
	Malaoxon	77	94	107	103	75	102

NA = not analysed
[1] Recoveries corrected for mean concurrent procedural recoveries <100%. Average procedural recoveries for raw agricultural commodities ranged from 82 to 99% for malathion and 91 to 111% for malaoxon

Table 27. Storage stability of malathion and malaoxon in processed commodities at <-5°C.

Sample	Analyte	Mean % recovery after nominal storage periods (months)[1]				
		0	1	3	6	12
Cotton seed						
Meal	Malathion	78	104	105	102	106
	Malaoxon	87	104	97	94	90
Hulls	Malathion	71	96	85	99	93
	Malaoxon	82	92	88	85	86
Oil	Malathion	78	103	94	97	97
	Malaoxon	91	91	103	102	95
Wheat						
Bran	Malathion	95	91	105	87	101
	Malaoxon	80	84	95	84	83
Flour	Malathion	102	104	104	100	104
	Malaoxon	105	102	110	116	99
Middlings	Malathion	92	94	118	90	98
	Malaoxon	84	96	106	87	91
Shorts	Malathion	96	91	101	103	102
	Malaoxon	96	90	96	99	98
Tomato						
Pomace	Malathion	101	102	98	112	101
	Malaoxon	104	103	105	105	101
Ketchup	Malathion	89	98	99	110	102
	Malaoxon	102	85	104	124	103

Sample	Analyte	Mean % recovery after nominal storage periods (months)[1]				
		0	1	3	6	12
Juice	Malathion	87	99	94	101	102
	Malaoxon	87	93	93	117	101

[1] Recoveries corrected for mean concurrent procedural recoveries <100%. Average procedural recoveries for processed commodities ranged from 69% to 105% for malathion and 92% to 111% for malaoxon.

USE PATTERN

Table 28 shows the registered uses of malathion in the crops discussed in this evaluation and the countries in which they are grown as of February 1998.

Table 28. Registered uses of malathion (if not indicated, application by foliar spray, from the ground and in the field; ai = active ingredient; EC= emulsible concentrate; ULV= ultra low volume).

Crop	Country	Form.	Application rate				PHI, days
			No.	kg ai/ha	Water l/ha	kg ai/hl	
Alfalfa	USA	EC		1.2-1.96	112		
		ULV		0.5-1.1			0-5
Apples	Australia	EC				0.06	3
	UK	EC				0.057-0.114	4
	USA	EC		0.8-1.6	3370/22[1]		3
		EC		2.7-20	1123-8987/225-1125		3
		EC		3.2-6.4	4494	0.07-0.14	3
		EC	12			0.11-0.16	4
Apricots	UK	EC				0.057-0.114	4
	USA	EC		1.6	2246/22[1]		7
		EC		5.4-12	1123-8987/225-1125		7
		EC		3.6-4.8	3370	0.1-0.14	7
		ULV		0.7-1.4			0
Asparagus	USA	EC		1.2-1.6	112		1
		EC		1.7	225-675/>56		1
Avocados	USA	EC		4.6-10	225-675/>56		7
		EC		3.6	3370	0.1	7
Beans	Australia	EC				0.06-0.1	3
	UK	EC		1.26	600		4
	USA	EC		1.6-2.0	112		1
		EC		1.7-2.4	225-675/>56		1
		ULV		0.7			1
Beans, Broad	Poland	EC	1-2	0.30	200-600	0.05-0.15	7
Beans, Dry	USA	EC		1.2-1.6			1
		ULV		0.7			1
Blackberries	UK	EC		0.00168		0.075	4
	USA	EC		2.4	2246/22[1]		1
		EC		2.4	2247	0.1	1
		EC		1.3-4.6	225-675/>56		1
Blueberries	USA	EC		1.2-2.6	2246/22[1]		1
		EC		1.7-2.8	225-675/>56		1
		EC		0.8-1.6	1123-2247	0.07	1
		ULV		0.8			0
Brassica vegetables	Thailand	EC		0.42-1.25	1000	0.042-0.125	
Broccoli	USA	EC		0.1-1.6	112		3
		EC		2.0-3.4	225-675/>56		3
Cabbages	Australia	EC				0.06-0.1	3
	Poland	EC	1-2	0.3-0-0.375	200-600	0.05-0.19	7
	USA	EC		0.1-1.6	112		7

Crop	Country	Form.	Application rate				PHI, days
			No.	kg ai/ha	Water l/ha	kg ai/hl	
		EC		2.0-3.4	225-675/>56		7
		EC				0.06-1.0	3
Carrots	Australia	EC				0.06-0.1	3
	Poland	EC	1-4	0.3-0.375	200-600	0.05-0.19	7
	UK	EC		1.26	600		4
	USA	EC		1.2-1.6	112		7
		EC		1.1-2.2	225-675/>56		7
Celery	Australia	EC				0.06-0.1	3
	UK	EC		1.26	600		4
	USA	EC		1.2	112		7
		EC		1.3-2.0	225-675/>56		7
Cereals	Australia	EC		0.24-1.1			1
		ULV		0.24-0.88			1
		EC				1.2	[5]
Cherries	UK	EC				0.075-0.114	4
	USA	EC		0.8-1.2	2246/22[1]		3
		EC		3.4-10	1123-8987/225-1125		3
		EC		3.2-4.8	4494	0.07-0.1	3
		ULV		1.0-1.3			1
Chestnuts	USA	EC		0.6	2246/22		0
		EC		2.7-6.8			
Citrus	Australia	EC				0.06-0.1	3
	Thailand	EC		0.042-0.125	5	0.002-0.006	3
	USA	EC		1.0-1.6	1123/22[1]		7
		EC		1.1-28.4	934-7476		7
		EC				0.06-0.1	3
Clover	USA	EC		1.2-1.6	112		
		ULV		0.7-1.0			
Corn	USA	EC		1.3	225-675/>56		5
		ULV		0.266-0.533			5
Corn, Field	USA	EC	3-5	1.2-1.6			5
		ULV		0.266-0.533			5
Corn, Sweet	USA	EC		1.2	112		5
	Thailand	EC		0.83	500	0.166	-
Cotton	USA	EC		0.4-3.14			
		ULV		0.3-1.4			0
Cucumbers	USA	EC		1.2	112		1
		EC		1.3-2.3	225-675/>56		3
		EC		1.2-1.6			1
Cucurbits	Australia	EC				0.03-0.1	3
		ULV		0.53-1.06			3
Figs	USA	EC		2.7	3370/22[1]		3
		EC		3.3	1123-8987/225-1125		3
Fruit trees	Australia	EC				0.05-1.25	3
	Poland	EC	2-3	0.625	500-1000	0.06-0.125	7
Grapes	Australia	EC				0.06-0.1	3
	USA	EC		1.2	2246-3089		3
		EC		2.3-3.1	1123-8987/225-1125		3
		EC		1.2-2.4	562-2247	0.1-0.2	3
		EC				0.06-0.1	3
Grass	USA	EC		1.2-1.6	112		
		ULV		0.5-0.8			
Guavas	USA	EC		1.0	1123-8987/225-1125		2
Herbs (except Celery leaves and Parsley)	Netherlands	EC EC	1-3 1-3	0.07-0.03	200-800	0.037	10/14 4
Lettuce	Australia	EC				0.06-0.1	3
	UK	EC		1.26	600		4

Crop	Country	Form.	Application rate				PHI, days
			No.	kg ai/ha	Water l/ha	kg ai/hl	
	USA	EC		1.6-2.4	112		7/14[2]
		EC		1.7-2.7	225-675/>56		7/14[2]
		EC	12			0.11-0.16	4
Macadamia nuts	USA	EC		4.0-20	1123-8987/225-1125		0
		EC		Up to 16.7		0.0013	
Maize	*see* Corn						
Mangoes	USA	EC		1.0	1123-8987/225-1125		2
	Thailand	EC		0.655-1.942	1560	0.042-0.125	3
Melons	USA	EC		1.2-2.3			1
Mint	USA	EC		1.2-1.6	112		7
Mushrooms	Netherlands	EC	2-5	1.25	2500	0.5	7
	USA	EC		1.9		0.13	1
Mustard greens	USA	EC		0.8-1.6	112		7
Okra	USA	EC		1.2-1.9	112		1
		EC		2.0	225-675/>56		1
Onions	Australia	EC				0.09	3
	Poland	EC	1-2	0.3-0.375	200-600	0.06-0.19	7
	UK	EC		1.26	600		4
	USA	EC		1.3-2.7	225-675/>56		3
Onions, including greens	USA	EC		1.2-2.4	112		3
Papayas	USA	EC				0.10-0.14	
Peaches	Australia	EC				1.05-1.06	
	UK	EC				0.057-0.114	4
	USA	EC		1.6	2246/22[1]		7
		EC		3.3-12	1123-8987/225-1125		7
		EC		1.8-4.8	1286-3370	0.14	7
Pears	Australia	EC				0.06	3
	UK	EC				0.057-0.114	4
	USA	EC		0.8-1.6	3370/22[1]		1
		EC		2.7-20	1123-8987/225-1125		1
		EC		2.4-4.8	3370	0.07-0.14	1
		EC	12			0.11-0.16	4
Peas	Australia	EC		0.63			3
		ULV		0.65			3
	Poland	EC	1-2	0.3	200-600	0.05-0.15	7
	UK	EC		1.26	600		4
	USA	EC		1.2-1.6	112		3
		EC		1.3-3.3	225-675/>56		3
		ULV		0.7			14
Peppers	USA	EC		1.0-1.2	112		3
		EC		1.0-2.0	225-675/>56		3
		EC	12			0.11-0.16	4
Pome fruit	Australia	ULV		0.53-0.66			3
	USA	EC				0.06	3
Potatoes	UK	EC		1.26	600		4
	USA	EC		0.8-1.2	112		0
		EC		1.1-3.3	225-675/>56		0
Raspberries	Poland	EC	1-2	0.625	750-1000	0.06-0.085	-
	UK	EC		0.00168-0.00252		0.075-0.114	4
	USA	EC		1.2-2.4	2246/22[1]		1
		EC		1.3-4.6	225-675/>56		1
		EC		2.4	2247	0.1	1
Rice	Australia	EC	1	0.3			
		ULV		0.82-0.83			
	Thailand	EC		0.311-0.415	375-500	0.083	-
	USA	EC		0.8-2.0	112		7
		EC		2.0	225-675/>56		7

Crop	Country	Form.	Application rate				PHI, days
			No.	kg ai/ha	Water l/ha	kg ai/hl	
		ULV		0.7			7
Sorghum	Australia	ULV		0.65-1.06			
	USA	EC		1.2	112		7
		ULV		0.7-1.0			7
Spinach	Poland	EC	1-2	0.3	200-600	0.05-0.15	7
	USA	EC		1.6	112		7
		EC		1.3-2.7	225-675/>56		7
Stone fruit	Australia	EC				0.06	3
		ULV		0.53-1.06			3
Strawberries	Poland	EC	1-2	0.625	750-1000	0.06-0.085	7
	USA	EC		1.2-2.4	2246/22[1]		3
		EC		1.3-2.7	225-675/>56		3[3]
		EC	12			0.11-0.16	4
Strawberries, currants, other berries and small fruits	Netherlands	EC	1-4	0.19-0.45	500-1200	0.0375	4
Sweet corn	*see* Corn						
Tomatoes	Australia	EC				0.06-0.1	3
	Poland	EC	1-2	0.3	200-600	0.05-0.15	7
	USA	EC		1.3-2.3	225-675/>56		3
		EC		2.3-4.0			5
		EC	12			0.11-0.16	4
		ULV		0.2-0.7			1
Turnips	USA	EC		0.8-1.6	112		3/7[4]
Vegetables	Netherlands	EC	1-3	0.07-0.30	200-800	0.037	4
		EC/G	1-3	0.19-0.56	500-1500	0.037	3/10/14
	Poland	EC	1-2	0.3-0-0.45	200-600	0.05-0.225	7
Walnuts	USA	EC		1.18-3.14	4672		
Watercress	USA	EC		1.3-2.7	225-675/>56		7
Wheat	USA	EC		1.2-1.7	112		7
		EC		1.7	225-675/>56		7
		EC				2.4	[5]
		ULV		0.3-0.7			7

[1]air application
[2]7 days for head lettuce and 14 days for leaf lettuce
[3]may also be incorporated in soil before planting
[4] in case tops are to be used for food or feed
[5]storage bin

RESIDUES RESULTING FROM SUPERVISED TRIALS

All the trials were in the USA. The results are shown in Tables 29 to 68. All samples were analysed for malathion and malaoxon. Trials with the same entry in the Tables were carried out at the same site. Some trials included sub-plots, separated from each other by a sufficient distance to avoid the possibility of contamination by spray drift. Residues from sub-plots under exactly the same application regime were regarded as being from one trial and the highest residue was considered for estimations of maximum residues levels and STMRs. Replicate analyses of the same samples were averaged and the mean result recorded. Unless otherwise indicated, all trials were conducted outdoors by foliar ground spray. Underlined residues were within maximum GAP (± 30%) and were considered for estimating MRL and STMR.

Oranges. In six trials in California and Florida with ground application of an EC formulation with 3 x 7 kg ai/ha, residues of malathion at 7 days PHI ranged from 0.42 to 1.90 mg/kg. In eight trials with aerial or ground application of a ULV formulation at or above the proposed label rate (10 x 0.196 kg ai/ha) residues ranged from <0.01 to 2.9 mg/kg (Table 29).

Table 29. Residues of malathion and oxon in oranges (whole fruit).

State Year	Form.	Application No.	Application kg ai/ha	Application kg ai/hl	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
California 1992 AA920117	EC	3	7	0.312	7	0.42	0.02	CA3
					14	0.43	0.02	
					7	1.9	<0.01	CA1
					14	2.4	0.01	
					7	1.3	0.02	CA2
					14	0.5	0.02	
	ULV aerial	10	0.196	29.2	1	0.05	<0.01	CA3
					7	0.08	<0.01	
					14	0.02	<0.01	
					1	0.03	<0.01	CA1
					7	<0.01	<0.01	
					14	<0.01	<0.01	
					1	0.03	<0.01	CA2
					7	0.02	<0.01	
					14	0.03	<0.01	
Florida 1992 AA920117	EC	3	7	0.312	7	0.75	<0.01	FL2
					14	0.26	<0.01	
					7	1.0	0.01	FL1
					14	0.64	0.02	
					7	0.79	0.02	FL3
					14	0.4	0.01	
	ULV aerial	10	0.196	29.2	1	<0.01	<0.01	FL2
					7	<0.01	<0.01	
					14	<0.01	<0.01	
					1	0.02	<0.01	FL1
					7	<0.01	<0.01	
					14	0.01	<0.01	
					1	<0.01	<0.01	FL3
					7	<0.01	<0.01	
					14	<0.01	<0.01	
05142.94	ULV	4	0.8		1	2.9	<0.05	FL25
					7	2.2	<0.05	
					1	2.5	<0.05	FL26
					7	0.54	<0.05	

Apples. In four trials on apples at 1.4 kg ai/ha, residues of malathion at 2 to 3 days after the last application were 0.05 to 2.6 mg/kg. In one trial at a fivefold rate the residue was 2.5 mg/kg (Table 30).

Table 30. Residues of malathion and oxon in apples (Study 04768).

State Year	Application No.	Application kg ai/ha	Sample	PHI, days	Residues, mg/kg Malathion	Residues, mg/kg Malaoxon	Reference
WA	5	1.4	Whole fruit	2	0.32, 0.19	<0.05. <0.05	WA51, WA52
TN	5	1.4	Whole fruit	3	2.64	0.08	TN07
CA	5	1.4	Whole fruit	3	0.05	<0.05	CA77
MI	5	1.4	Whole fruit	3	0.14	<0.05	MI31
NY	5	1.4	Whole fruit	2	0.28	<0.05	NY26
	5	7	Whole fruit	2	2.5	<0.05	NY26
			Juice		0.33	<0.05	
			Pomace		10	0.07	

Pears. In three trials on pears, residues of malathion at a PHI of 1 day ranged from 0.34 to 1.9 mg/kg (Table 31).

Table 31. Residues of malathion and oxon in pears (Study 04827), 1994.

State Year	Application			PHI, days	Residues, mg/kg		Reference
	No.	kg ai/ha	kg ai/hl		Malathion	Malaoxon	
CA	5	1.4		1	1.9	0.33	CA79
NY	5	1.4		1	0.59	<0.05	NY27
WA	5	1.4		1	0.34	<0.05	WA53

Cherries. In twelve trials on sweet and tart cherries with 6 ground or aerial applications malathion residues at 1 or 3 days PHI ranged from 0.02 to 2.6 mg/kg (Table 32).

Table 32**.** Residues of malathion and oxon in cherries.

State Year	Form	Application			PHI, days	Residues, mg/kg		Reference
		No.	kg ai/ha	kg ai/hl		Malathion	Malaoxon	
Sweet cherries								
CA, 1993	EC	6	2x 1.12 4x 8.96		3 7 14	1.8 0.24 0.09	0.01 <0.01 <0.01	CA1
	ULV aerial	6	1.366		1 4 7 14	0.08 0.13 0.19 0.09	<0.01 <0.01 <0.01 <0.01	
OR, 1993	EC	6	4.2		3 7 14	0.45 0.51 0.05	<0.01 <0.01 <0.01	OR1
	ULV aerial	6	1.366		1 4 7 14	0.17 0.06 0.05 0.03	<0.01 <0.01 <0.01 <0.01	
MI, 1993	EC	6	4.2		3 7 14	0.26 0.05 <0.01	<0.01 <0.01 <0.01	MI1
	ULV aerial	6	1.366		1 4 7 14	0.02 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	
Tart Cherries								
MI, 1993	EC	6	4.2		3 7 14	2.6 0.41 0.05	0.02 <0.01 <0.01	MI1
	ULV aerial	6	1.366		1 4 7 14	0.03 0.02 0.01 <0.01	<0.01 <0.01 <0.01 <0.01	
MT, 1993	EC	6	4.2		3 7 14	1.6 0.43 0.18	<0.01 <0.01 <0.01	MT1
	ULV aerial	6	1.366		1 4 7 14	0.47 0.23 0.13 0.05	<0.01 <0.01 <0.01 <0.01	
NY, 1993	EC	6	4.2		3 7 14	1.1 0.03 <0.01	<0.01 <0.01 <0.01	NY1
	ULV aerial	6	1.366		1 4 7 14	0.34 0.42 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	

Apricots and peaches. In one trial on apricots and four on peaches, residues of malathion at a PHI of 6-7 days varied from 0.16 to 1.4 mg/kg (Table 33).

Table 33. Residues of malathion and oxon in apricots and peaches (whole fruit).

State	Application		PHI,	Residues, mg/kg		
	No.	kg ai/ha	days	Malathion	Malaoxon	Reference
Apricots						
CA	4	4.2	6	0.60	<0.05	
Peaches[1]						
CA	4	4.2	7	0.16	<0.05	CA53
GA	5	4.2	7	0.25	<0.05	GA2
MI	4	4.2	7	1.2	<0.05	MI11
NJ	4	4.2	7	1.4	<0.05	NJ11

[1]Sampling to analysis 845-905 days; checked storage stability 469 days

Grapes. In six trials on grapes at 1.2-3.1 kg ai/ha, residues of malathion at a PHI of 3 days ranged from 0.33 to 2.7 mg/kg (Table 34).

Table 34. Residues of malathion and oxon in grapes (whole fruit).

State Year	PHI, days	Residues, mg/kg Malathion	 Malaoxon	 Reference
CA 1992	3 7 14	0.33 0.14 0.10	<0.01 <0.01 <0.01	CA1
1993	3 7 14	1.2 0.52 0.41	0.02 0.03 0.04	CA2
	3 7 14	0.78 0.98 0.32	0.03 0.05 0.04	CA3
	3 7 14	2.7 1.7 0.49	0.13 0.12 0.06	CA4
WA 1993	3 7 14	0.94 0.69 0.81	0.01 <0.01 0.01	WA1
NY 1992	3 7 14	0.58 0.19 0.22	<0.01 <0.01 <0.01	NY1

Strawberries. Seven trials on strawberries using an EC or WP formulation were within GAP rates (1.3-2.7 kg ai/ha). Residues of malathion at 3 days PHI ranged from 0.09 to 0.59 mg/kg (Table 35).

Table 35. Residues of malathion and oxon in strawberries (whole fruit).

State Year	 Form	Application No.	 kg ai/ha	PHI, days	Residue, mg/kg Malathion	 Malaoxon	 Reference
CA 1993	EC	6	2.2	3 7 14	0.25 0.07 0.05	0.05 <0.01 <0.01	AA920122.CA1,
	EC	6	2.2	3 7 14	0.39 0.31 0.12	0.01 0.03 <0.01	AA920122.CA2
1992	EC	6	2.1	3	0.53	<0.05	05152.92
	WP	6	2.24	3	0.59	0.063	05152.92

State Year	Form	Application No.	Application kg ai/ha	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
FL 1993	EC	6	2.2	3 7 14	0.19 0.02 0.01	<0.01 <0.01 <0.01	AA920122.FL1
OR 1993	EC	6	2.2	3 7 14	0.16 0.05 0.04	<0.01 <0.01 <0.01	AA920122.OR1
PA 1993	EC	6	2.2	3 7 14	0.09 0.01 0.02	<0.01 <0.01 <0.01	AA920122.PA1

Berries. In eleven trials on blueberries using ground or aerial application, residues of malathion at 0-1 day varied from 0.06 to 7.5 mg/kg (Table 36).

In 6 trials on blackberries and in 4 on raspberries with WP or EC formulations, residues of malathion at a 1-day PHI varied from 1.3 to 11 mg/kg. (Table 36).

Table 36. Residues of malathion and oxon in berries.

State	Form	Application No.	Application kg ai/ha	Application kg ai/hl	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
Blueberries (Study No. AA920105)								
MI	EC	4	1.4		1 4 7 14	1.4 0.09 0.08 0.04	0.02 <0.01 <0.01 <0.01	MI1
	EC	4	1.4		1 4 7 14	0.26 0.05 0.04 0.01	0.03 <0.01 <0.01 <0.01	MI2
	ULV aerial	5	0.71		0 4 7 14	0.55 0.05 0.15 0.02	<0.01 <0.01 <0.01 <0.01	MI1
	ULV aerial	5	0.71		0 4 7 14	0.06 <0.01 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	MI2
ME	EC	4	1.4		1 4 7 14	3.2 0.56 0.32 0.32	0.05 0.03 0.02 0.02	ME1
	EC	4	1.4		1 4 7 14	7.1 2.2 1.0 0.76	0.14 0.10 0.07 0.05	ME2
	EC	7	0.751		0 4 7 14	2.8 0.39 0.16 0.14	0.03 0.01 0.01 0.01	ME2
	ULV aerial	5	0.877		0 4 7 14	4.0 0.43 0.18 0.07	0.02 <0.01 <0.01 <0.01	ME1
	ULV aerial	5	0.877		0 4 7 14	7.5 0.51 0.24 0.45	0.03 0.01 0.01 0.02	ME2

State	Form	Application			PHI, days	Residue, mg/kg		Reference
		No.	kg ai/ha	kg ai/hl		Malathion	Malaoxon	
OR	EC	4	1.4		1	0.29	0.03	OR1
					4	0.12	0.01	
					7	0.09	<0.01	
					14	0.02	<0.01	
	EC	4	1.4		1	1.2	0.03	OR2
					4	0.31	0.01	
					7	0.13	<0.01	
					14	0.09	<0.01	
Blackberries (Study No. 04774)								
CA	EC	4	2.1		1	2.0	0.05	CA82
	WP	4	2.24		1	1.6	0.04	CA82
OR	EC	4	2.27		1	3.9	0.06	OR14
	WP	4	2.24		1	11[1]	0.11	OR14
	EC	4	2.27		1	2.6	0.04	OR18
	WP	4	2.24		1	3.4	0.05	OR18
Raspberries (Study No. 4835)								
WA	EC	4	2.24		1	2.6	0.07	WA[1]40
	WP	4	2.24		1	1.3	0.06	WA[1]40
	EC	4	2.24		1	4.7	0.07	WA[1]39
	WP	4	2.24		1	4.9	0.07	WA[1]39

[1]Three other replicate samples had residues of 2.1, 2.7 and 3.3 mg/kg. Result calculation was based on peak response more than 10% outside the calibration range.

Assorted tropical and sub-tropical fruits. In two trials on avocados, two on figs, three on guavas, one on sugar apples, one on mangoes and three on papayas, malathion residues 1 to 7 days after the last application ranged from <0.05 to 0.56 mg/kg (Table 37).

Table 37. Residues of malathion and oxon in assorted tropical fruits.

State Year	Application		PHI, days	Residue, mg/kg		Reference
	No.	kg ai/ha		Malathion	Malaoxon	
Avocado (Study No. AA92102)						
CA, 1993	2	5.264	7	0.08	<0.01	CA1
			14	0.05	<0.01	
	2	5.264	7	0.07	<0.01	CA2
			14	0.05	<0.01	
Fig (Study No. 04793)						
CA, 1992	1	2.8	5	0.32	<0.05	4793
	3	2.8	5	0.36	<0.05	4793
					<0.05	
Guava (Study No. 04799)						
Hawaii, 1933	12	1.4	2	0.30	0.18	HI01
			7	0.13	0.09	
FL, 1993	13	1.4	2	0.24	<0.05	FL21
			7	0.12	<0.05	
FL, 1995	11	1.4	1	0.10	<0.05	FL06
			6	<0.05	<0.05	
Papaya (Study No. 03727)						
Hawaii, 1993	12	1.4	1	0.56	<0.05	HI02
			7	0.11	<0.05	
FL, 1993	12	1.4	1	0.06	<0.05	FL07
			7	<0.05	<0.05	
FL, 1994	12	1.4	1	<0.05	<0.05	FL53
			7	<0.05	<0.05	
Sugar apple						
FL, 1994	8	1.4	3	0.31	<0.05	
			7	0.08	<0.05	

State Year	Application No.	Application kg ai/ha	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
Mango (Study No. B4814)						
FL, 1995	8	1.4	1 6	0.07, <0.05, <0.05 <0.05	<0.05 (3) <0.05	Fl09, FL08, FL07

Onions. In six trials on bulb onions and six on green onions (bulb including the leaves), residues of malathion at 3 days PHI ranged from 0.02 to 0.59 mg/kg in bulb onions and from 0.18 to 5.0 mg/kg in green onions (Table 38).

Table 38. Residues of malathion and oxon in onions.

State Year	Application Form	Application kg ai/ha	PH, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
Bulb onions (Study No. AA920115)						
CA		5 X 1.74	3	0.08	<0.01	Study No.° AA
	EC		7	0.03	<0.01	920115 CA1
1993			14	0.02	<0.01	
			3	0.35	0.02	Study No.° AA920115 CA2
			7	0.42	0.02	
			14	0.23	0.02	
NE	EC	5 X 1.74	3	0.37	<0.01	Study No.° AA920115 NE1
			7	0.16	<0.01	
1993			14	0.05	<0.01	
NY	EC	5 X 1.74	3	0.59	<0.01	Study No.° AA920115 NY1
			7	0.24	<0.01	
1993			14	0.11	<0.01	
OR	EC	5 X 1.74	3	0.02	<0.01	Study No.° AA920115 OR1
			7	<0.01	<0.01	
1992			14	<0.01	<0.01	
TX	EC	5 X 1.74	3	0.11	<0.01	Study No.° AA920115 TX1
			7	0.03	<0.01	
1993			14	<0.01	<0.01	
Green onions (Study No. AA920116)						
CA	EC	5 X 1.74	3	5.0	0.02	Study No. AA920116 CA1
			7	0.97	0.01	
1993			14	0.27	<0.01	
			3	0.18	0.02	Study No. AA920116 CA2
			7	0.17	0.01	
			14	0.02	<0.01	
NE	EC	5 X 1.74	3	0.19	<0.01	Study No. AA920116 NE1
			7	0.01	<0.01	
1993			14	<0.01	<0.01	
NY	EC	5 X 1.74	3	0.35	<0.01	Study No. AA920116 NY1
			7	0.23	<0.01	
1993			14	0.03	<0.01	
OR	EC	5 X 1.74	3	2.5	0.02	Study No. AA920116 OR1
			7	0.22	<0.01	
1992			14	0.02	<0.01	
TX	EC	5 X 1.74	3	0.69	0.03	Study No. AA920116 TX1
			7	0.11	<0.01	
1993			14	<0.01	<0.01	

Broccoli. In five trials on broccoli, malathion residues from 3 to 5 days after the last application varied from 0.02 to 9.3 mg/kg (Table 39).

Table 39. Residues of malathion and oxon in broccoli.

State	Application	PHI,	Residue, mg/kg	

Year	Form	No.	kg ai/ha	days	Malathion	Malaoxon	Reference
NY 1992	EC	6	1.4	4	0.02	<0.02	NY22
1994		5	1.4	5	0.02	<0.02	NY12
TN 1992	EC	5	1.4	3	9.3	0.13	TN04
WA 1992	EC	6	1.4	3	0.10	0.02	WA28
CA 1992	EC	5	1.4	2	0.31	<0.02	CA34

Cabbage. In 8 trials on head cabbages, samples taken with and without the wrapper leaves at 7 days PHI had residues of malathion of <0.05 mg/kg, with the exception of one trial with a residue of 0.10 mg/kg (Table 40).

Table 40**.** Residues of malathion and oxon in cabbages.

State Year	Sample	Application Form	Application kg ai/ha	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
FL 1992	with wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 FL48
	without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	
WA 1992	with wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 WA22
	without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	
OH 1992	with wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 OH17
	without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	
WI 1992	with and without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 WI09
IN 1992	with and without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 IN05
NR 1992	with wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 NY21
	without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	
TX 1992	with wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 TX37
	without wrapper leaves	EC	6 x 1.4	7	0.10	<0.05	
CA 1992	with wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	Study No. 04778 CA57
	without wrapper leaves	EC	6 x 1.4	7	<0.05	<0.05	

Cucumber. In nine trials on cucumbers, malathion residues at a 1 day PHI ranged from <0.01 to 0.10 mg/kg (Table 41).

Table 41. Residues of malathion and oxon in cucumbers.

State Year	Application Form	Application kg ai/ha	PHI, days	Residues, mg/kg Malathion	Residues, mg/kg Malaoxon	Reference
CA	EC	3 x 2.1	1	0.02	<0.01	Study No. AA920111 CA1
1992/1993			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
FL	EC	3 x 2.1	1	≤0.01	<0.01	Study No. AA920111 FL1
1992/1993			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	

State Year	Application Form	kg ai/ha	PHI, days	Residues, mg/kg Malathion	Malaoxon	Reference
MI 1992/1993	EC	3 x 2.1	1	0.10	<0.01	Study No. AA920111 MI1
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
	EC	3 x 2.1	1	0.02	<0.01	Study No. AA920111 MI2
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
NC 1992/1993	EC	3 x 2.1	1	0.03	<0.01	Study No. AA920111 NC1
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
	EC	3 x 2.1	1	0.01	<0.01	Study No. AA920111 NC2
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
NJ 1992/1993	EC	3 x 2.1	1	0.02	<0.01	Study No. AA920111 NJ1
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
TX 1992/1993	EC	3 x 2.1	1	0.06	<0.01	Study No. AA920111 TX1
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
	EC	3 x 2.1	1	0.03	<0.01	Study No. AA920111 TX2
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	

Melons. In two trials on cantaloupes and one trial on watermelons residues at 1 day ranged from <0.05 to 0.80 mg/kg (Table 42).

Table 42. Residues of malathion and oxon in cantaloupes and watermelons.

State Year	Application Form	kg ai/ha	PHI, days	Residue, mg/kg Malathion	Malaoxon	Reference
Cantaloupe						
CA 1992	EC	6 x 1.12	1	<0.05	<0.05	Study No. 04815
TX 1992	EC	6 x 1.12	1	0.80	0.05	Study No. 04815
Watermelon						
GE 1992	EC	6 x 1.12	1	<0.05	<0.05	Study No. 04815

Mushrooms. In one trial with two sub-plots on mushrooms in Pennsylvania in 1994, malathion was applied four times as an EC formulation at the GAP rate 1.9 kg ai/ha. No residues of malathion or malaoxon were detected (<0.05 mg/kg) at a PHI of 1 day.

Peppers. In seven trials on bell peppers residues of malathion at 3 days ranged from <0.01 to 0.08 mg/kg (Table 43).

Table 43. Residues of malathion and oxon in bell peppers.

State Year	Application Form	kg ai/ha	PHI, days	Residue, mg/kg Malathion	Malaoxon	Reference

State Year	Application Form	Application kg ai/ha	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
CA 1992/1993	EC	5 x 1.8	3	0.05	<0.01	CA1
			7	<0.01	<0.01	
			14	<0.01	<0.01	
	EC	5 x 1.8	3	0.08	<0.01	CA2
			7	<0.01	<0.01	
			14	<0.01	<0.01	
FL 1992/1993	EC	5 x 1.8	3	≤0.01, <0.01	<0.01, <0.01	FL1, FL2
			7	<0.01, <0.01	<0.01, <0.01	
			14	<0.01, <0.01	<0.01, <0.01	
MI 1992/1993	EC	5 x 1.8	3	0.02	<0.01	MI1
			7	<0.01	<0.01	
			14	<0.01	<0.01	
NC 1992/1993	EC	5 x 1.8	3	≤0.01	<0.01	NC1
			7	<0.01	<0.01	
			14	<0.01	<0.01	
NJ 1992/1993	EC	5 x 1.8	3	≤0.01	<0.01	NJ1
			7	<0.01	<0.01	
			14	<0.01	<0.01	
TX 1992/1993	EC	5 x 1.8	3	≤0.01	<0.01	TX1
			7	<0.01	<0.01	
			14	<0.01	<0.01	

Tomatoes. In fourteen trials on tomatoes at 1.74 or 3.84 kg ai/ha the growth stage at final application was mature fruit, early maturity or late flowering. Residues of malathion at a PHI of 1 day varied from 0.10 to 1.2 mg/kg and at a higher rate from 0.13 to 1.2 mg/kg (Table 44).

Table 44**.** Residues of malathion and oxon in tomatoes (EC formulations).

State Year	Application No.	Application kg ai/ha	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
CA 1993	5	1.74	1	0.21	<0.01	CA1
			3	0.16	<0.01	
			7	0.04	<0.01	
			14	0.01	<0.01	
	5	1.74	1	0.10	<0.01	CA2
			3	0.07	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
	5	1.74	1	0.33	<0.01	CA3
			3	0.13	<0.01	
			7	0.06	<0.01	
			14	0.32	<0.01	
	5	3.84	3	0.70	<0.01	CA1
			7	0.16	<0.01	
			14	0.03	<0.01	
	5	3.84	3	0.13	<0.01	CA2
			7	0.02	<0.01	
			14	<0.01	<0.01	
	5	3.84	3	0.73	<0.01	CA3
			7	0.15	<0.01	
			14	0.03	<0.01	
FL 1992	5	1.74	1	0.14	<0.01	FL1
			3	0.12	<0.01	
			7	0.02	<0.01	
			14	<0.01	<0.01	
	5	3.84	3	0.73	<0.01	
			7	0.05	<0.01	
			14	<0.01	<0.01	

State Year	Application No.	Application kg ai/ha	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
MI 1993	5	1.74	1 3 7 14	0.27 0.05 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	MI1
	5	1.74	1 3 7 14	0.17 0.08 <0.01 <0.01	<0.01 <0.01 <0.01 <0.01	MI2
	5	3.84	3 7 14	0.23 0.05 <0.01	<0.01 <0.01 <0.01	MI1
	5	3.84	3 7 14	0.54 0.03 <0.01	<0.01 <0.01 <0.01	MI2
NJ 1992	5	1.74	1 3 7 14	0.41 0.19 0.05 <0.01	<0.01 0.01 <0.01 <0.01	NJ1
	5	3.84	3 7 14	1.2 0.15 0.01	0.05 <0.01 <0.01	

Sweet corn. Twelve trials were conducted on sweet corn with either ground application of an EC formulation or aerial application of a ULV formulation. After five days malathion residues in the kernels and cobs ranged from <0.01 to 0.02 mg/kg, and in the forage from <0.05 to 2.4 mg/kg from ground applications and from 0.06 to 41 mg/kg from aerial applications (Table 45).

Table 45. Residues of malathion and oxon in sweet corn.

State Year	Application Form	Application No.	Application kg ai/ha	Sample	PHI, days	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
CA 1993	EC	5	1.4	Kernel + cob	5 14	≤0.01 <0.01	<0.01 <0.01	CA1
	EC	5	1.4	Forage	5 14	2.4 1.0	0.21 0.12	
	ULV (aerial)	5	0.683	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	
	ULV (aerial)	5	0.683	Forage	5 14	41 17	0.19 0.11	
FL 1993	EC	5	1.4	Kernel + cob	5 14	≤0.01 <0.01	<0.01 <0.01	FL1
	EC	5	1.4	Forage	5 14	0.20 <0.05	<0.05 <0.05	
	ULV (aerial)	5	0.683	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	
	ULV (aerial)	5	0.683	Forage	5 14	0.12 <0.05	<0.05 <0.05	
MN 1993	EC	5	1.4	Kernel + cob	5 14	≤0.01 <0.01	<0.01 <0.01	MN1
	EC	5	1.4	Forage	5 14	1.7 0.09	<0.05 <0.05	
	ULV (aerial)	5	0.683	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	
	ULV (aerial)	5	0.683	Forage	5 14	19 1.6	<0.05 <0.05	
NY 1992	EC	5	1.4	Kernel + cob	5 14	≤0.01 <0.01	<0.01 <0.01	NY1
	EC	5	1.4	Forage	5 14	0.33 <0.05	<0.05 <0.05	

State Year	Application			Sample	PHI, days	Residue, mg/kg		Reference
	Form	No.	kg ai/ha			Malathion	Malaoxon	
	ULV (aerial)	5	0.683	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	
	ULV (aerial)	5	0.683	Forage	5 14	6.9 1.3	<0.05 <0.05	
WA 1993	EC	5	1.4	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	WA1
	EC	5	1.4	Forage	5 14	<0.05 <0.05	<0.05 <0.05	
	ULV (aerial)	5	0.683	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	
	ULV (aerial)	5	0.683	Forage	5 14	0.06 <0.05	<0.05 <0.05	
WI 1993	EC	5	1.4	Kernel + cob	5 14	0.02 <0.01	<0.01 <0.01	WI1
	EC	5	1.4	Forage	5 14	<0.05 <0.05	<0.05 <0.05	
	ULV (aerial)	5	0.683	Kernel + cob	5 14	<0.01 <0.01	<0.01 <0.01	
	ULV (aerial)	5	0.683	Forage	5 14	0.67 <0.05	<0.05 <0.05	

Okra. In two trials on okra, malathion residues at 1 day were <0.05 and 2.1 mg/kg (Table 46).

Table 46**.** Residues of malathion and oxon in okra.

State year	Application			PHI, days	Residue, mg/kg		Reference
	Form	No.	kg ai/ha		Malathion	Malaoxon	
TX 1992	EC	4 +2	1.68	3 1	<0.05 <0.05	0.10 0.05	Study No. 04820
SC 1994	EC	4 +2	1.68	2 1	0.12 2.1	<0.05 <0.05	

Lettuce. In six trials on leaf lettuce, malathion residues at a PHI of 14 days ranged from <0.01 to 3.1 mg/kg in samples with and without the wrapper leaves. Residues in head lettuce 14 days after the last application (the recommended PHI is 7 days) ranged from 0.01 to 0.17 mg/kg (Table 47).

Table 47**.** Residues of malathion and oxon in lettuce.

State Year	Application		PHI, days	Residue, mg/kg		Reference
	Form	kg ai/ha		Malathion	Malaoxon	
Leaf leattuce						
CA 1992	EC	6 x 2.1	7 14	3.3 0.99	<0.01 <0.01	Study No. AA920114 CA1
1993	EC	6 x 2.1	7 14	16 3.1	0.24 0.08	Study No. AA920114 CA2
AZ	EC	6 x 2.1	7 14	0.04 <0.01	<0.01 <0.01	Study No. AA920114[1] AZ1
FL	EC	6 x 2.1	7 14	<0.01 <0.01	<0.01 <0.01	Study No. AA920114[1] FL1
NJ	EC	6 x 2.1	7 14	0.04 <0.01	<0.01 <0.01	Study No. AA920114[1] NJ1
WA	EC	6 x 2.1	7 14	0.10 <0.01	<0.01 <0.01	Study No. AA920114[1] WA1
Head lettuce						
CA 1992	EC	6 x 2.1	14 21	0.06 0.16	<0.01 <0.01	Study No. AA920126 CA1
1993	EC	6 x 2.1	14 21	0.17 0.07	0.04 0.03	Study No. AA920126 CA2

State Year	Application		PHI,	Residue, mg/kg		
	Form	kg ai/ha	days	Malathion	Malaoxon	Reference
	EC	6 x 2.1	14	0.01	<0.01	Study No. AA920126 CA3
			21	<0.01	<0.01	

[1] wrapper leaves were removed before analysis

Mustard greens. In seven trials on mustard greens at 1.23 or 1.4 kg ai/ha, malathion residues at 7 days ranged from <0.05 to 1.1 mg/kg. In seven other trials at twice these rates residues ranged from <0.05 to 5.9 mg/kg (Table 48).

Table 48. Residues of malathion and oxon in mustard greens.

State	Application			PHI,	Residue, mg/kg		Reference
Year	Form	No.	kg ai/ha	days	Malathion	Malaoxon	
AZ	EC	6	1.23	7	0.46	<0.05	Study No. 04817
1992		3	2.45	7	0.59	<0.05	
CA	EC	6	1.4	7	0.07	<0.05	Study No. 04817
1992		3	2.8	7	0.05	0.07	
GA	EC	6	1.4	7	0.52	<0.05	Study No. 04817
1992		3	2.8	7	2.6	<0.05	
IN	EC	6	1.4	9	<0.05	0.06	Study No. 04817
1992		3	2.8	9	<0.05	0.10	
NC	EC	3	1.4	7	0.07	0.07	Study No. 04817
1992							
SC	EC	6	2.8	6	3.2	0.08	Study No. 04817
1992							
TX	EC	6	1.4	7	1.1	<0.05	Study No. 04817
1993		3	2.8	7	5.9	0.10	
WA	EC	6	1.4	7	<0.05	<0.05	Study No. 04817
1992		3	2.8	7	<0.05	<0.05	

Spinach. In five trials on spinach according to GAP (1.3-2.7 kg ai/ha), malathion residues at a PHI of 7 days ranged from <0.05 to 2.2 mg/kg. One trial gave a residue of 36 mg/kg (Table 49).

Table 49. Residues of malathion and oxon in spinach.

State	Application		PHI,	Residues, mg/kg		Reference
Year	Form	kg ai/ha	days	Malathion	Malaoxon	
NJ	EC	3 x 2.24[1]	7	36	<0.05	Study No. 04842
1992/1995			7	0.35	<0.05	Study No. 04842
WA 1992	EC	3 x 2.24	7	<0.05	<0.05	Study No. 04842
CA 1993	EC	3 x 2.24	7	0.16	<0.05	Study No. 04842
TX 1993	EC	3 x 2.24	7	2.2	<0.05	Study No. 04842
SC 1995	EC	3 x 2.24	7	1.1	<0.05	Study No. 04842

[1]Rate based on field notes. Actual rate was probably much higher, in view of the malathion residue

Watercress. In three trials on watercress, residues of malathion were <0.05 mg/kg in samples taken at 3 and 7 days (Table 50).

Table 50. Residues of malathion and oxon in watercress.

State	Application				PHI,	Residue, mg/kg	
Year	Form	No.	kg ai/ha	type	days	Malathion	Malaoxon
FL	EC	5	1.4	spray	3	<0.05	<0.05
					7	<0.05	<0.05

State Year	Application				PHI, days	Residue, mg/kg	
	Form	No.	kg ai/ha	type		Malathion	Malaoxon
	EC	5	1.4	chemigation	3	<0.05	<0.05
					7	<0.05	<0.05
HW	EC	2	0.5	spray	7	<0.05	<0.05

Beans. Ten trials on lima beans and snap beans by aerial application at the GAP rate (0.7 kg ai/ha) gave malathion residues at a PHI of 1 day from <0.01 to 0.90 mg/kg (Table 51).

Table 51. Residues of malathion and oxon in lima and snap beans from aerial application of an ULV formulation at 3 x 0.683 kg ai/ha (samples included the pods).

State Year	PHI, days	Residue, mg/kg		Reference
		Malathion	Malaoxon	
Lima beans (Study N° AA920125)				
CA	1	0.90	0.02	CA1
1993	4	0.44	<0.01	
	7	0.08	<0.01	
	14	0.01	<0.01	
	1	0.05	<0.01	CA2
	4	<0.01	<0.01	
	7	<0.01	<0.01	
	14	<0.01	<0.01	
NC	1	0.71	<0.01	NC1
1993	4	0.52	<0.01	
	7	0.02	<0.01	
	14	<0.01	<0.01	
PA	1	0.49	<0.01	PA1
1993	4	0.16	<0.01	
	7	0.13	<0.01	
	14	<0.01	<0.01	
WI	1	0.41	<0.01	WI1
1992	4	0.03	<0.01	
	7	0.02	<0.01	
	14	<0.01	<0.01	
Snap beans (Study N° AA9200103)				
FL	1	≤0.01	<0.01	FL1
1993	4	<0.01	<0.01	
	7	<0.01	<0.01	
	14	<0.01	<0.01	
NY	1	0.13	<0.01	NY1
1993	4	<0.01	<0.01	
	7	0.03	<0.01	
	14	<0.01	<0.01	
OR	1	0.56	<0.01	OR1
1993	4	0.07	<0.01	
	7	0.01	<0.01	
	14	0.24	<0.01	
WI	1	0.12	<0.01	WI1
1992	4	0.01	<0.01	
	7	<0.01	<0.01	
	14	<0.01	<0.01	
1993	1	0.21	<0.01	WI2
	4	<0.01	<0.01	
	7	<0.01	<0.01	
	14	<0.01	<0.01	

Peas. Three trials on peas using EC formulations were at 5 x 2.8 kg ai /ha. Malathion residues in peas with pods at 2 to 3 days ranged from 0.34 to 0.96 mg/kg and in dry forage from 2.9 to 32 mg/kg (Table 52).

Table 52 Residues of malathion and oxon in peas with pods.

State year	Application Form	Application kg ai/ha	PHI, days	Sample	Residue, mg/kg Malathion	Residue, mg/kg Malaoxon	Reference
CA 1992	EC	5 x 2.8	3	Peas with pods	0.96	0.08	4823.92-CA*22
			3	Fresh forage	18	0.22	
			3	Dry forage	32	0.51	
1994	EC	5 x 2.8	2	Peas with pods	0.34	<0.02	4823.94-CA*42
			7	Fresh forage	10	<0.02	
			13	Dry forage	14	<0.02	
WI 1992	EC	5 x 2.8	3	Peas with pods	0.38	0.04	4823.92-WI03
			3	Fresh forage	5.3	0.10	
			3	Dry forage	2.9	0.08	

Dry beans. In ten trials on dry beans with two aerial applications according to GAP (0.7 kg ai/ha) malathion residues ranged from 0.01 to 1.2 mg/kg at a PHI of one day or longer (Table 53).

Table 53**.** Residues of malathion and oxon in dry beans.

State Year	Application Form	Application kg ai/ha	PH, days	Residues, mg/kg Malathion	Residues, mg/kg Malaoxon	Reference
CA 1993	ULV	3 x 0.683	1	0.62	<0.01	Study No. AA920104 CA1
			4	0.34	0.02	
			7	0.45	0.02	
			14	0.23	<0.01	
	ULV	3 x 0.683	1	0.73	0.02	Study No. AA920104 CA2
			4	1.2	0.07	
			7	0.38	0.01	
			14	0.12	<0.01	
	ULV	3 x 0.683	1	0.42	<0.01	Study No. AA920104 CA3
			4	0.16	<0.01	
			7	0.28	<0.01	
			14	0.39	<0.01	
ID 1993	ULV	3 x 0.683	1	0.39	<0.01	Study No. AA920104 ID1
			4	0.29	0.01	
			7	0.02	<0.01	
			14	0.13	<0.01	
MI 1992	ULV	3 x 0.683	1	0.36	<0.01	Study No. AA920104 MI1
			4	0.04	<0.01	
			7	<0.01	<0.01	
			14	<0.01	<0.01	
1993	ULV	3 x 0.683	1	0.05	<0.01	Study No. AA920104 MI2
			4	<0.01	<0.01	
			7	<0.01	<0.01	
			14	0.01	<0.01	
	ULV	3 x 0.683	1	0.07	<0.01	Study No. AA920104 MI3
			4	0.02	<0.01	
			7	<0.01	<0.01	
			14	0.01	<0.01	
NE 1993	ULV	3 x 0.683	1	<0.01	<0.01	Study No. AA920104 NE1
			4	<0.01	<0.01	
			7	0.10	<0.01	
			14	<0.01	<0.01	
	ULV	3 x 0.683	1	<0.01	<0.01	Study No. AA920104 NE2
			4	0.02	<0.01	
			7	<0.01	<0.01	
			14	0.10	<0.01	
NY 1993	ULV	3 x 0.683	1	0.05	<0.01	Study No. AA920104 NY1
			4	<0.01	<0.01	
			7	0.16	<0.01	
			14	<0.01	<0.01	

Potatoes. In fifteen trials on potatoes with EC formulations at 1.74 kg ai/ha with two applications, malathion residues were <0.01 mg/kg in all but one sample at a 0 day PHI (Table 54).

Table 54. Residues of malathion and oxon in potatoes.

State Year	Application		PHI, days	Residue, mg/kg		Reference
	Form	kg ai/ha		Malathion	Malaoxon	
CA 1993	EC	2 x 1.74	0	<0.01	<0.01	Study No. AA920119 CA1
ID 1993	EC	2 x 1.74	0	<0.01	<0.01	Study No. AA920119 ID1
			0	<0.01	<0.01	Study No. AA920119 ID2
			0	<0.01	<0.01	Study No. AA920119 ID3
			0	<0.01	<0.01	Study No. AA920119 ID4
			0	<0.01	<0.01	Study No. AA920119 ID5
			0	<0.01	<0.01	Study No. AA920119 ID6
			0	<0.01	<0.01	Study No. AA920119 ID7
			0	<0.01	<0.01	Study No. AA920119 ID8
ME 1993	EC	2 x 1.74	0	<0.01	<0.01	Study No. AA920119 ME1
			0	<0.01	<0.01	Study No. AA920119 ME2
			0	<0.01	<0.01	Study No. AA920119 ME3
			0	<0.01	<0.01	Study No. AA920119 ME4
NE 1993	EC	2 x 1.74	0	<0.01	<0.01	Study No. AA920119 NE1
WI 1993	EC	2 x 1.74	0	0.02	<0.01	Study No. AA920119 WI1

Turnips. In trials on turnips with EC formulations at 1.4 kg ai/ha or SC at 2.35-2.8 kg ai/ha malathion residues in tops ranged from <0.05 to 3.4 mg/kg and in roots from <0.05 to 0.13 mg/kg at 7 days. In one trial at a higher rate (South Carolina), residues in tops were 15 and 10 mg/kg and in roots 0.11 mg/kg (Table 55).

Table 55**.** Residues of malathion and oxon in turnips.

State Year	No. of	PHI, days	Sample	Residue, mg/kg		Reference
				Malathion	Malaoxon	
GA	3	7	Tops	0.66	<0.05	GA[1]26
1992	+2	7	Tops	1.4	<0.05	
			Roots	0.09	<0.05	
OH	3	7	Tops	<0.05	<0.05	OH[1]18
1992	+2	7	Tops	<0.05	<0.05	
			Roots	<0.05	<0.05	
TX	3	7	Tops	1.8	<0.05	TX[1]38
1992	+2	7	Tops	0.89	<0.05	
			Roots	<0.05	<0.05	
WA	3	7	Tops	<0.05	<0.05	WA[1]27
1992	+2	7	Tops	0.99	<0.05	
			Roots	<0.05	<0.05	
CA	3	7	Tops	0.63	<0.05	CA[1]13
1993	+2	7	Tops	3.4	<0.05	
			Roots	0.13	<0.05	
IN	5	7	Tops	<0.05	<0.05	IN07
1994			Roots	<0.05	<0.05	
SC	3	7	Tops	15	0.11	SC[1]01
1993	+2	7	Tops	10	<0.05	
			Roots	0.11	<0.05	

Carrots. In six trials on carrots with an EC formulation at 1.4 kg ai/ha, malathion residues ranged from <0.05 to 0.54 mg/kg at 6-8 days (Table 56).

Table 56**.** Residues of malathion and oxon in carrots.

State	No. of	PHI,	Residue, mg/kg

			Malathion	Malaoxon
CA 1994 [1]	7	7	0.36	<0.05
FL 1994	9	8	<0.05	<0.05
NJ 1994	7	6	0.11	<0.05
TX 1994	7	7	0.54	<0.05
WA 1994	7	7	0.12	<0.05
WI 1994	7	7	<0.05	<0.05

[1]application rates were calculated from spray swath rather than row width (55% lower)

Celery. In two trials on celery in Florida and California, malathion was applied as an EC formulation at 3 x 1.68 kg ai/ha (Study N°. 04781), which is within GAP (1.2-2.0 kg ai/ha). Residues of malathion at 7 days were 0.91 and 1.2 mg/kg and of malaoxon <0.05 mg/kg.

Asparagus. In four trials on asparagus with EC formulations at 9 x 1.4 kg ai/ha, malathion residues ranged from 0.10 to 0.69 mg/kg at a one day PHI (Table 57).

Table 57. Residues of malathion and oxon in asparagus.

State Year	Application		Residue, mg/kg		Reference
	Form	kg ai/ha	Malathion	Malaoxon	
CA, 1994/1995	EC	9 x 1.4	0.69	<0.05	Study No. 04770
NJ, 1994/1995	EC	9 x 1.4	0.48	<0.05	
WA, 1994/1995	EC	9 x 1.4	0.10	<0.05	
WI, 1994/1995	EC	9 x 1.4	0.13	<0.05	

Wheat. Twenty two trials on winter and spring wheat according to GAP were with either ground applications of EC or aerial applications of ULV formulations. Malathion residues at a PHI of 7 days ranged from <0.01 to 0.28 mg/kg in grain, from <0.05 to 2.4 mg/kg in forage, and from <0.05 to 34 mg/kg in straw (Table 58).

Table 58**.** Residues of malathion and oxon in wheat.[1]

State year	Application				Sample	PHI, days	Residues, mg/kg		Reference
	Form	No.	kg ai/ha	kg ai/hl			Malathion	Malaoxon	
Winter wheat (Study N° AA920127)									
KS 1993	EC	3	1.4		Grain	7	0.04	<0.01	KS1
						14	0.02	<0.01	
					straw	7	1.6	<0.05	
						14	1.2	<0.05	
	EC	3	1.4		Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
	EC	3	1.4		Grain	7	0.04	<0.01	KS2
						14	0.01	<0.01	
					straw	7	0.66	<0.05	
						14	0.36	<0.05	
	EC	3	1.4		Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	

State year	Application				Sample	PHI, days	Residues, mg/kg		Reference
	Form	No.	kg ai/ha	kg ai/hl			Malathion	Malaoxon	
	ULV (aerial)	3	0.683		Grain	7	0.04	<0.01	KS1
						14	0.06	<0.01	
					straw	7	6.5	<0.05	
						14	3.9	<0.05	
	ULV (aerial)	3	0.683		Forage	7	0.49	<0.05	
						14	0.29	<0.05	
	ULV (aerial)	3	0.683		Grain	7	0.04	<0.01	KS2
						14	0.03	<0.01	
					straw	7	7.2	<0.05	
						14	1.2	<0.05	
	ULV (aerial)	3	0.683		Forage	7	1.9	<0.05	
						14	1.7	<0.05	
MT	EC	3	1.4		Grain	7	0.08	<0.01	MT1
						14	0.02	<0.01	
					straw	7	0.68	<0.05	
						14	0.35	<0.05	
	EC	3	1.4		Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	0.08	<0.01	
						14	0.02	<0.01	
					straw	7	3.2	<0.05	
						14	1.2	<0.05	
	ULV (aerial)	3	0.683		Forage	7	0.27	<0.05	
						14	<0.05	<0.05	
OH	EC	3	1.4		Grain	7	<0.01	<0.01	OH1
						14	<0.01	<0.01	
					straw	7	<0.05	<0.05	
						14	<0.05	<0.05	
	EC	3	1.4		Forage	7	0.09	0.05	
						14	<0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	0.03	<0.01	
						14	0.36	<0.01	
					straw	7	1.6	<0.05	
						14	2.0	<0.05	
	ULV (aerial)	3	0.683		Forage	7	0.23	<0.05	
						14	<0.05	<0.05	
OK	EC	3	1.4		Grain	7	0.10	<0.01	OK1
						14	0.02	<0.01	
					straw	7	2.2	<0.05	
						14	0.29	<0.05	
	EC	3	1.4		Forage	7	0.05	<0.05	
						14	<0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	0.20	<0.01	OK2
						14	0.05	<0.01	
					straw	7	12	<0.05	
						14	10	<0.05	
	ULV (aerial)	3	0.683		Forage	7	2.3	<0.05	
						14	0.36	<0.05	
	ULV (aerial)	3	0.683		Grain	7	0.28	<0.01	
						14	0.09	<0.01	
					straw	7	5.1	<0.05	
						14	12	<0.05	
	ULV (aerial)	3	0.683		Forage	7	1.8	<0.05	
						14	2.3	<0.05	
WA	EC	3	1.4		Grain	7	0.03	<0.01	WA1
						14	0.02	<0.01	
					straw	7	3.2	0.13	
						14	1.3	<0.05	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	

State year	Application				Sample	PHI, days	Residues, mg/kg		Reference
	Form	No.	kg ai/ha	kg ai/hl			Malathion	Malaoxon	
	ULV (aerial)	3	0.683		Grain	7	<u>≤0.01</u>	<0.01	
						14	<0.01	<0.01	
					straw	7	<u>1.0</u>	0.06	
						14	0.15	<0.05	
					Forage	7	<u>≤0.05</u>	<0.05	
						14	<0.05	<0.05	
Spring wheat (Study N° AA92124)									
ND	EC	3	1.4		Grain	7	<u>0.02</u>	<0.01	ND1
						14	0.02	<0.01	
					straw	7	<u>2.5</u>	<0.05	
						14	1.4	<0.05	
	EC	3	1.4		Forage	7	<u>≤0.05</u>	<0.05	
						14	<0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<u>0.10</u>	<0.01	
						14	0.04	<0.01	
					straw	7	<u>18</u>	<0.05	
						14	21	<0.05	
	ULV (aerial)	3	0.683		Forage	7	<u>1.3</u>	<0.05	
						14	0.33	<0.05	
	EC	3	1.4		Grain	7	<u>0.04</u>	<0.01	ND2
						14	0.03	<0.01	
					straw	7	<u>0.81</u>	<0.05	
						14	1.0	<0.05	
	EC	3	1.4		Forage	7	<u>≤0.05</u>	<0.05	
						14	<0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<u>0.22</u>	<0.01	
						14	0.23	<0.01	
						7	<u>8.4</u>	<0.05	
					straw	14	5.4	<0.05	
	ULV (aerial)	3	0.683		Forage	7	<u>0.19</u>	<0.05	
						14	0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<u>0.09</u>	<0.01	ND3
						14	0.07	<0.01	
					straw	7	<u>34</u>	0.08	
						14	31	0.08	
	ULV (aerial)	3	0.683		Forage	7	<u>2.4</u>	<0.05	
						14	0.91	<0.05	
WA	EC	3	1.4		Grain	7	<u>0.14</u>	<0.01	WA1 (A)
						14	0.05	<0.01	
					straw	7	<u>9.4</u>	0.29	
						14	3.8	0.13	
	EC	3	1.4		Forage	7	<u>≤0.05</u>	<0.05	WA1
						14	<0.05	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<u>≤0.01</u>	<0.01	WA1 (A)
						14	<0.01	<0.01	
					straw	7	<u>1.4</u>	0.05	
						14	0.41	<0.05	
	ULV (aerial)	3	0.683		Forage	<u>7</u>	<0.05	<0.05	WA1
						14	<0.05	<0.05	

[1]Separate plots were sampled for forage and grain/straw

One trial was conducted in 1994 in Illinois to measure the residues in grain treated post-harvest with malathion. The storage bin was treated with 2.4 kg ai/hl of an EC formulation according to GAP and the wheat grain received an application of 8 g ai/1000 l grain of a dust formulation during and after bin loading, followed by two other treatments with the dust formulation. The malathion residue in the grain after 59 days of storage was 7.5 mg/kg (Table 59).

Table 59**.** Residues of malathion and oxon in wheat grain after post-harvest treatment.

Treatment	PHI, days	Residues, mg/kg	
		Malathion	Malaoxon
1 x 4 g ai/1000 l grain immediately after transfer to storage bin	0	50	<0.01
1 x 4 g ai/1000 l grain after 59 days of storage	59	7.5	<0.01

Sorghum. Eight trials on sorghum were with either ground application of an EC formulation or aerial application of a ULV formulation. Malathion residues in the grain at 7 days ranged from 0.02 to 2.2 mg/kg (Table 60).

Table 60**.** Residues of malathion and oxon in sorghum grain.

State Year	Application			PHI, days	Residue, mg/kg		Reference
	Form	No.	kg ai/ha		Malathion	Malaoxon	
NE 1993	EC	3	1.4	7	0.07	<0.01	Study No. AA920121 NE1
				14	<0.01	<0.01	
	EC	3	1.4	7	0.02	<0.01	Study No. AA920121 NE2
				14	0.01	<0.01	
	ULV (aerial)	3	0.683	7	0.34	<0.01	Study No. AA920121 NE1
				14	0.30	<0.01	
	ULV (aerial)	3	0.683	7	0.10	<0.01	Study No. AA920121 NE2
				14	0.13	<0.01	
TX 1993	EC	3	1.4	7	0.49	<0.01	Study No. AA920121 TX1
				14	0.36	<0.01	
	EC	3	1.4	7	0.12	<0.01	TX2
				14	0.04	<0.01	
	ULV (aerial)	3	0.683	7	2.2	0.08	Study No. AA920121 TX1
				14	1.5	0.06	
	ULV (aerial)	3	0.683	7	2.0	<0.01	Study No. AA920121 TX2
				14	0.79	<0.01	

Maize. Twenty one trials on field corn according to GAP were with either ground application of an EC formulation (GAP is 1.2 -1.6 kg ai/ha) or aerial application of a ULV formulation (GAP is 0.266-0.533 kg ai/ha). Malathion residues after 7 days (GAP PHI is 5 days) were <0.01 to 0.02 mg/kg in grain, <0.05 to 1.2 mg/kg in forage and 1.3 to 24 mg/kg in straw (Table 61).

Table 61. Residues of malathion and oxon in maize.

County Year	Formulation	Application			Sample	PHI, days	Residues, mg/kg		Reference
		No.	kg ai/ha	kg ai/hl			Malathion	Malaoxon	
IA 1992/ 1993	EC	3	1.4		Grain	7	0.01	<0.01	IA1
						14	<0.01	<0.01	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
					Straw	7	1.3	<0.05	
						14	1.2	0.08	
	EC	3	1.4		Grain	7	0.02	<0.01	IA2
						14	<0.01	<0.01	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
					Straw	7	3.4	0.10	
						14	3.0	0.19	

County Year	Formulation	Application No.	kg ai/ha	kg ai/hl	Sample	PHI, days	Residues, mg/kg Malathion	Malaoxon	Reference
	EC	3	1.4		Grain	7	0.02	<0.01	IA3
						14	<0.01	<0.01	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
					Straw	7	3.2	0.07	
						14	2.5	0.12	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IA1
						14	<0.01	<0.01	
					Forage	7	0.06	<0.05	
						14	<0.05	<0.05	
					Straw	7	2.0	<0.05	
						14	5.0	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IA2
						14	<0.01	<0.01	
					Forage	7	0.09	<0.05	
						14	0.06	<0.05	
					Straw	7	4.5	<0.05	
						14	6.7	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IA3
						14	<0.01	<0.01	
					Forage	7	1.2	<0.05	
						14	0.16	<0.05	
					Straw	7	8.0	<0.05	
						14	6.5	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IA4
						14	<0.01	<0.01	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
					Straw	7	1.4	<0.05	
						14	0.81	<0.05	
IL 1992/ 1993	EC	3	1.4		Grain	7	0.02	<0.01	IL1
						14	<0.01	<0.01	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
					Straw	7	4.7	0.08	
						14	2.3	0.10	
	EC	3	1.4		Grain	7	<0.01	<0.01	IL2
						14	<0.01	<0.01	
					Forage	7	<0.05	<0.05	
						14	<0.05	<0.05	
					Straw	7	1.8	0.06	
						14	5.2	0.23	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IL1
						14	<0.01	<0.01	
					Forage	7	0.22	<0.05	
						14	<0.05	<0.05	
					Straw	7	24	0.07	
						14	18	0.12	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IL2
						14	<0.01	<0.01	
					Forage	7	0.15	<0.05	
						14	<0.05	<0.05	
					Straw	7	4.8	<0.05	
						14	6.6	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<0.01	<0.01	IL3
						14	<0.01	<0.01	
					Forage	7	0.21	<0.05	
						14	0.34	<0.05	
					Straw	7	22	0.07	
						14	12	0.06	

County Year	Formulation	Application No.	kg ai/ha	kg ai/hl	Sample	PHI, days	Residues, mg/kg Malathion	Malaoxon	Reference
NE 1992/ 1993	EC	3	1.4		Grain	7	<u>≤0.01</u>	<0.01	NE1
						14	<0.01	<0.01	
					Forage	7	<u>0.12</u>	<0.05	
						14	<0.05	<0.05	
					Straw	7	<u>2.3</u>	0.07	
						14	0.66	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<u>0.02</u>	<0.01	NE1
						14	<0.01	<0.01	
					Forage	7	0.17	<0.05	
						14	<u>0.24</u>	<0.05	
					Straw	7	<u>13</u>	0.05	
						14	3.3	<0.05	
	ULV (aerial)	3	0.683		Grain	7	<u>≤0.01</u>	<0.01	NE2
						14	<0.01	<0.01	
					Forage	7	<u>0.76</u>	<0.05	
						14	0.28	<0.05	
					Straw	7	<u>6.9</u>	0.05	
						14	4.0	<0.05	
OH 1992/ 1993	EC	3	1.4		Grain	7	<u>≤0.01</u>	<0.01	OH1
						14	<0.01	<0.01	
					Forage	7	<u>0.19</u>	<0.05	
						14	<0.05	<0.05	
					Straw	7	9.9	0.13	
						14	<u>11</u>	0.22	
	ULV (aerial)	3	0.683		Grain	7	<u>≤0.01</u>	<0.01	
						14	0.01	<0.01	
					Forage	7	<u>0.09</u>	<0.05	
						14	<0.05	<0.05	
					Straw	7	<u>11</u>	0.05	
						14	6.3	0.05	
TX 1992/ 1993	EC	3	1.4		Grain	7	<u>≤0.01</u>	<0.01	TX1
						14	<0.01	<0.01	
					Forage	7	<u>≤0.05</u>	<0.05	
						14	<0.05	<0.05	
					Straw	7	3.1	0.09	
						14	<u>4.5</u>	0.13	
	ULV (aerial)	3	0.683		Grain	7	<u>≤0.01</u>	<0.01	
						14	<0.01	<0.01	
					Forage	7	<u>0.07</u>	<0.05	
						14	<0.05	<0.05	
					Straw	7	4.6	<0.05	
						14	<u>12</u>	0.11	
WI 1992/ 1993	EC	3	1.4		Grain	7	<u>≤0.01</u>	<0.01	WI1
						14	<0.01	<0.01	
					Forage	7	<u>≤0.05</u>	<0.05	
						14	<0.05	<0.05	
					Straw	7	13	0.23	
						14	<u>19</u>	0.73	
	ULV (aerial)	3	0.683		Grain	7	<u>≤0.01</u>	<0.01	
						14	<0.01	<0.01	
					Forage	7	<u>0.25</u>	<0.05	
						14	0.07	<0.05	
					Straw	7	<u>12</u>	0.15	
						14	7.3	0.07	

One trial was conducted to determine the residues in maize grain treated post-harvest with malathion. The storage bin was treated with 2.4 kg ai/hl of an EC formulation according to GAP and the grain received an application of 8g ai/1000 l grain of a dust formulation during and after bin loading. Two other treatments were made with dust formulation (Table 62). Malathion residues in grain after 60 days of storage were 6.9 mg/kg.

Table 62. Residues of malathion and oxon in maize grain after post-harvest treatment.

Treatment	PHI, days	Residue, mg/kg	
		Malathion	Malaoxon
1 x 4g ai/1000 litre grain immediately after transfer to storage bin	0	80	0.02
1 x 4g ai/1000 litre grain after 60 days of storage	60	6.9	0.03

Nuts. In two trials on chestnuts**,** malathion residues at a PHI of 2 days were 0.08 and 0.58 mg/kg. In two trials on macadamia nuts and two on walnuts, no residues (<0.05 mg/kg) were detected after a 1- or 7-day PHI in samples with and without the shells (Table 63). The labels state that application to the three types of nuts may be at harvest.

Table 63. Residues of malathion and oxon in nuts treated with EC formulations.

State Year	Application		Sample	PHI, days	Residue, mg/kg	
	No.	kg ai/ha			Malathion	Malaoxon
Chestnut (Study N°. A4783)						
FL 1995	4	5.6	Hulls removed	2	0.58	<0.05
	4	5.6	Hulls removed	2	0.08	<0.05
Macadamia nuts (Study N° 04812)						
HW 1992	7	1.0	Hulls and shell removed	1	<0.05	<0.05
	7	1.0	Hulls and shell removed	1	<0.05	<0.05
Walnuts (Study N° 04851)						
CA, 1992	3	2.8	Hulls and shell removed	7	<0.05	<0.05
1995	3	2.8	Hulls and shell removed	7	<0.05	<0.05

Cotton. Seventeen trials on cotton were with ground applications of EC formulations or air applications of ULV and ready-to-use (RTU) formulations. Malathion residues in cotton seed at a 0 or 1 day PHI ranged from 2.1 to 14 mg/kg (Table 64).

Table 64. Residues of malathion and oxon in cotton.

State Year	Application			PHI, days	Residue, mg/kg		Reference
	Form	No.	kg ai/ha		Malathion	Malaoxon	
AZ 1993	EC	25	2.8	0	4.1	0.06	Study No. AA920110 AZ1
				1	3.9	0.06	
				4	2.4	<0.05	
				7	1.8	0.13	
				14	3.0	0.37	
	Ready-to-use (aerial)	25	1.3	0	4.2	0.10	
				1	1.5	0.07	
				4	2.1	0.11	
				7	1.3	0.14	
				14	3.3	0.34	
CA 1993	E C	25	2.8	0	5.6	0.06	Study No. AA920110 CA1
				1	5.9	0.06	
				4	5.2	0.06	
				7	1.8	<0.05	
				14	0.23	<0.05	
	E C	25	2.8	0	14	0.12	Study No. AA920110 CA2
				1	7.1	0.07	
				4	7.6	0.10	
				7	4.3	0.06	
				14	4.2	0.06	
	ULV aerial	25	1.4	0	5.4	<0.05	Study No. AA920110 CA1
				1	5.4	<0.05	
				4	2.1	<0.05	
				7	2.0	<0.05	
				14	1.2	<0.05	

State Year	Application			PHI,	Residue, mg/kg		
	Form	No.	kg ai/ha	days	Malathion	Malaoxon	Reference
	ULV (aerial)	25	1.4	0 1 4 7 14	5.6 7.1 4.0 2.0 1.3	0.05 0.07 <0.05 <0.05 <0.05	Study No. AA920110 CA2
	Ready-to-use (aerial)	25	1.3	0 1 4 7 14	4.3 4.8 2.4 1.8 1.1	0.06 0.07 <0.05 <0.05 <0.05	Study No. AA920110 CA1
	Ready-to-use (aerial)	25	1.3	0 1 4 7 14	4.7 3.5 2.1 1.7 0.90	0.05 0.05 <0.05 <0.05 <0.05	Study No. AA920110 CA2
LA 1993	E C	25	2.8	0 1 4 7 14	7.8; 6.0 7.4; 4.7 2.3; 2.3 1.4; 1.2 1.4; 0.65	<0.05; <0.05 0.05; <0.05 <0.05; <0.05 <0.05; <0.05 <0.05; <0.05	Study No. AA920110 LA1; LA2
	ULV Aerial	25	1.4	0 1 4 7 14	2.1 2.1 0.48 0.40 0.14	<0.05 <0.05 <0.05 <0.05 <0.05	Study No. AA920110 LA1
	Ready-to-use (aerial)	25	1.3	0 1 4 7 14	5.4 1.9 0.50 0.74 0.25	0.07 0.07 <0.05 <0.05 <0.05	Study No. AA920110 LA2
TX 1192/1993	E C	25	2.8	0 1 4 7 14	3.8 3.1 2.1 0.66 0.73	0.07 0.07 0.10 <0.05 0.07	Study No. AA920110 TX1
	E C	25	2.8	0 1 4 7 14	3.0 2.9 2.4 2.9 2.1	0.08 0.09 0.09 0.12 0.12	Study No. AA920110 TX2
	ULV (aerial	25	1.4	0 1 4 7 14	6.4 3.2 2.0 2.1 1.4	0.10 0.06 0.07 0.06 0.07	Study No. AA920110 TX1
	ULV (aerial)	25	1.4	0 1 4 7 14	2.7 1.5 1.8 1.6 0.45	<0.05 <0.05 <0.05 0.06 0.06	Study No. AA920110 TX2
	Ready-to-use (aerial)	25	1.3	0 1 4 7 14	4.9 2.6 1.9 0.67 0.57	0.12 0.09 0.11 0.07 0.06	Study No. AA920110 TX1
	Ready-to-use (aerial)	25	1.3	0 1 4 7 14	1.8 2.3 0.92 0.87 0.36	<0.05 0.07 <0.05 0.05 0.05	Study No. AA920110 TX2

Flax. In one trial on flax in Nevada in 1994 (Study No. 04795) malathion was applied as an EC formulation at a proposed GAP rate of 1 x 0.56 kg ai/ha. Samples of straw, seed and meal were analysed. No residues of malathion or malaoxon were detected in any sample (<0.05 mg/kg) 52 days after application (the proposed GAP PHI is 45 days).

Mint. In three trials on mint, malathion residues at a PHI of 7 days ranged from 0.51 to 1.4 mg/kg in fresh mint and 5.7- 9.1 mg/kg in mint oil. In four trials at a fivefold rate the residues were 13-56 mg/kg in fresh mint and 140-460 mg/kg in oil (Table 65).

Table 65**.** Residues of malathion and oxon in peppermint and spearmint at 7 days PHI.

State year	Application			Sample analysed	Residues, mg/kg		Reference
	No.	kg ai/ha	kg ai/hl		Malathion	Malaoxon	
WI	3	1.1		Fresh peppermint	1.4	<0.05	Study No. 04829 WI15
1992	3	5.3		Fresh peppermint	56	0.12	
				Peppermint oil	460	0.10	
1993	3	1.1		Fresh peppermint	0.51	<0.05	Study No. 04829 WI19
				Peppermint oil	5.7	<0.05	
	3	5.3		Fresh peppermint	13	0.23	
				Peppermint oil	190	0.08	
IH	3	1.1		Peppermint oil	9.1	<0.05	Study No. 04829 IH15
1993	3	5.3		Peppermint oil	140	0.08	
	3	1.1		Fresh peppermint+spearmint[1]	1.2	0.10	Study No. 04829 IH14
				Spearmint oil	8.0	<0.05	
	3	5.3		Fresh peppermint+spearmint[1]	32	0.40	
				Spearmint oil	200	0.13	

[1]Composite sample from trials IH14 and IH15

Clover. Fourteen trials on clover were with ground application of an EC or aerial application of ULV formulation. The applications were made before each cutting. Malathion residues in clover forage at day 0 or later (GAP allows application at harvest) varied from 2.8 to 95 mg/kg. Residues in clover hay ranged from 4.4 to 120 mg/kg (Table 66).

Table 66. Residues of malathion and oxon in clover.

State Year	Application			Sample	PHI, days	Residue, mg/kg	
	Form	No.	kg ai/ha			Malathion	Malaoxon
GA	EC	2	1.4	Forage/hay	0	17/35	0.08/0.25
1993				1st cut	1	8.4/24	0.08/0.18
					4	8.0/14	0.11/0.14
					7	6.5/11	0.08/0.16
	ULV aerial	2	0.68	Forage/hay	0	33/34	0.06/0.17
				1st cut	1	28/24	0.09/0.18
					4	5.5/9.2	<0.05/0.07
					7	6.3/13	0.06/0.09
ID	EC	2	1.4	Forage/hay	0	71/21	0.10/0.22
				1st cut	1	7.5/10	<0.05/0.11
					4	2.5/7.0	<0.05/0.09
					7	2.4/6.6	<0.05/0.07
					14	0.68/2.9	<0.05/<0.05
				2nd cut	0	88/120	0.11/0.46
					1	44/74	0.11/0.30
					4	21/12	0.19/<0.05
					7	4.3/16	<0.05/0.07
					14	2.8/13	<0.05/0.06

State Year	Application			Sample	PHI, days	Residue, mg/kg	
	Form	No.	kg ai/ha			Malathion	Malaoxon
	ULV aerial	2	0.68	Forage/hay 1st cut	0	46/58	<0.05/0.35
					1	11/22	<0.05/0.18
					4	7.0/14	<0.05/0.11
					7	5.5/14	<0.05/0.09
					14	1.9/7.6	<0.05/<0.05
				2nd cut	0	56/98	0.05/0.27
					1	51/96	0.06/0.29
					4	45/30	0.11/0.06
					7	18/26	<0.05/0.06
					14	8.5/13	<0.05/0.06
MI	EC	2	1.4	Forage/hay 1st cut	0	20/16	<0.05/
					1	2.2/8.9	<0.05
					4	2.0/7.1	<0.05/<0.05
					7	2.0/3.0	<0.05/<0.05
					14	1.1/3.4	<0.05/<0.05
				2nd cut	0	37/64	<0.05/<0.05
					1	9.4/30	0.12/0.50
					4	3.1/11	<0.05/0.24
					7	2.6/4.3	<0.05/0.07
					14	2.5/4.8	<0.05/<0.05
				3rd cut	0	73/34	<0.05/<0.05
					1	32/49	0.13//0.25
					4	10/4.7	0.10/0.45
					7	3.1/7.2	<0.05/<0.05
					14	1.3/1.6	<0.05/0.05
							<0.05/<0.05
	ULV aerial	2	0.68	Forage/hay 1st cut	0	3.2/4.4	<0.05/<0.05
					1	0.39/0.48	<0.05/<0.05
					4	0.19/0.32	<0.05/<0.05
					7	0.10/0.32	<0.05<0.05
					14	0.12/0.14	<0.05/<0.05
				2nd cut	0	8.7/20	<0.05/0.16
					1	0.20/2.7	<0.05/<0.05
					4	0.09/1.7	<0.05/<0.05
					7	0.15/0.54	<0.05/<0.05
					14	0.12/0.20	<0.05/<0.05
				3rd cut	0	14/9.4	<0.05/0.08
					1	8.3/19	<0.05/0.20
					4	3.3/0.41	<0.05/<0.05
					7	0.69/1.7	<0.05/<0.05
					14	0.66/0.35	<0.05/<0.05
MN	EC	2	1.4	Forage/hay 1st cut	0	57/13	0.11/0.05
					1	22/15	<0.05/0.06
					4	12/18	<0.05/0.11
					7	5.6/13	<0.05/0.07
					14	4.9/5.0	<0.05/<0.05
	ULV aerial	2	0.68	Forage 1st cut	0	60/11	<0.05/<0.05
					1	52/12	<0.05<0.05
					4	56/93	0.16/0.29
					7	40/8.6	0.15/<0.05
					14	46/13	0.10/<0.05
NY	EC	2	1.4	Forage/hay 1st cut	0	36/5.7	<0.05/<0.05
					1	39/9.7	0.05/<0.05
					4	2.5/6.6	<0.05/<0.05
					7	3.9/21	<0.05/0.13
					14	2.8/7.5	<0.05/0.07
				2nd cut	0	95/86	0.11/0.32
					1	51/25	0.11/0.34
					4	11/15	0.05/0.12
					7	4.7/12	<0.05/0.09
					14	2.9/4.4	<0.05/0.07

State Year	Application			Sample	PHI, days	Residue, mg/kg	
	Form	No.	kg ai/ha			Malathion	Malaoxon
	ULV aerial	2	0.68	Forage/hay 1st cut	0	9.5/26	0.05/0.11
					1	4.8/22	<0.05/0.06
					4	3.9/9.7	<0.05/0.06
					7	1.2/5.8	<0.05/<0.05
					14	1.8/4.9	<0.05/<0.05
				2nd cut	0	16/18	<0.05/<0.05
					1	20/24	<0.05/0.09
					4	7.7/26	<0.05/0.15
					7	4.4/10	<0.05/0.07
					14	3.4/4.7	<0.05/<0.05
OK	EC	2	1.4	Forage/hay 1st cut	0	31/53	0.10/0.22
					1	9.4/20	<0.05/<0.05
					4	1.2/4.7	<0.05/<0.05
					7	0.71/2.1	<0.05/<0.05
					14	0.20/1.4	<0.05/<0.05
				2nd cut	0	18/36	0.07/0.21
					1	7.7/10	0.05/0.10
					4	1.5/2.6	0.05/0.10
					7	0.79/1.3	<0.05/<0.05
					14	0.47/0.97	<0.05/<0.05
	ULV aerial	2	0.68	Forage/hay 1st cut	0	25/90	<0.05/0.30
					1	24/55	<0.05/0.09
					4	11/22	<0.05/0.06
					7	7.2/16	<0.05/0.05
					14	0.83/5.3	<0.05/<0.05
				2nd cut	0	2.9/33	<0.05/0.16
					1	39/32	<0.05/0.10
					4	5.6/19	<0.05/0.15
					7	5.2/15	<0.05/0.07
					14	1.4/1.9	<0.05/<0.05
WI	EC	2	1.4	Forage/hay 1st cut	0	14/5.4	<0.05/<0.05
					1	7.8/9.2	<0.05/0.06
					4	2.0/12	<0.05/12
					7	0.74/2.5	<0.05/2.5
					14	0.37/1.1	<0.05/1.1
				2nd cut	0	40/80	<0.05/0.40
					1	27/90	<0.05/0.41
					4	7.1/13	<0.05/0.07
					7	6.4/20	<0.05/0.14
					14	3.1/8.7	<0.05/0.05
	ULV aerial	2	0.68	Forage 1st cut	0	2.8/3.3	<0.05/<0.05
					1	1.2/5.0	<0.05/<0.05
					4	0.95/3.9	<0.05<0.05
					7	1.6/4.0	<0.05/<0.05
					14	0.48/1.9	<0.05/<0.05
				2nd cut	0	38/93	<0.05/0.22
					1	26/84	<0.05/0.24
					4	13/35	<0.05/0.14
					7	11/42	0.05/0.23
					14	8.5/23	0.05/0.10

Alfalfa. Two series of eleven trials on alfalfa were with a ground application of either an EC or air application of a ULV formulation. The applications were made before each cutting. Malathion residues in alfalfa forage at day 0 (GAP allows application at harvest) were 0.99 to 98 mg/kg. Residues in hay (PHI 0 day or later) were 1.5 to 175 mg/kg (Table 67).

Table 67. Residues of malathion and oxon in alfalfa (Study No. AA920101).

State Year	Application				Sample analysed	PHI, days	Residue, mg/kg		Reference
	Form	No.	kg ai/ha				Malathion	Malaoxon	

State Year	Application Form	No.	kg ai/ha		Sample analysed	PHI, days	Residue, mg/kg Malathion	Malaoxon	Reference
CA 1993	EC	2	1.4		Forage/hay	0	51/6.1	0.13/<0.05	CA1
					1st cut	1	16/3.8	0.07/<0.05	
						4	2.9/0.93	0.11/<0.05	
					2nd cut	0	34/43	0.14/0.46	
						1	12/12	0.13/0.48	
						4	1.1/4.4	0.10/0.28	
					3rd cut	0	64/27	0.26/0.39	
						1	8.1/12	0.07/0.30	
						4	2.1/2.2	0.16/0.16	
	ULV aerial	2	0.68		Forage/hay	0	72/52	0.09/0.31	
					1st cut	1	34/79	0.07/0.43	
						4	9.5/19	0.06/0.14	
					2nd cut	0	43/26	<0.05/0.14	
						1	19/8.1	<0.05/0.22	
						4	8.7/26	<0.05/0.16	
					3rd cut	0	41/56	0.08/0.41	
						1	49/34	0.08/0.39	
						4	16/11	0.07/0.18	
IA 1993	EC	2	1.4		Forage/hay	0	51/	0.08	IA1
					1st cut	1	6.5/	<0.05	
						4	0.16/	<0.05	
					2nd cut	0	60/17	0.10/0.30	
						1	1.5/2.0	<0.05/<0.05	
						4	0.42/1.5	<0.05/<0.05	
					3rd cut	0	92/17	0.06/0.20	
						1	2.5/3.1	<0.05/0.07	
						4	1.2/1.3	<0.05/<0.05	
	ULV aerial	2	0.68		Forage/hay	0	23/20	<0.05/0.06	
					1st cut	1	9.8/19	<0.05/0.07	
						4	2.1/8.8	<0.05/<0.05	
					2nd cut	0	36/14	<0.05/<0.05	
						1	5.3/4.3	<0.05/<0.05	
						4	0.53/1.6	<0.05/<0.05	
					3rd cut	0	95/25	<0.05/0.05	
						1	6.3/7.5	<0.05/<0.05	
						4	7.8/10	<0.05/<0.05	
ID 1993	EC	2	1.4		Forage/hay	0	53/	0.08	ID1
					1st cut	1	24/	<0.05	
						4	1.4/	<0.05	
					2nd cut	0	94/140	0.11/0.64	
						1	95/89	0.14/0.53	
						4	30/34	0.13/0.57	
	ULV aerial	2	0.68		Forage/hay	0	20/12	<0.05/<0.05	
					1st cut	1	16/30	<0.05/0.07	
						4	1.1/3.5	<0.05/<0.05	
					2nd cut	0	25/67	<0.05/0.10	
						1	48/74	<0.05/0.28	
						4	21/66	<0.05/0.40	
MI 1993	EC	2	1.4		Forage/hay	0	28/	0.06	MI1
					1st cut	1	40/	<0.05	
						4	14/	<0.05	
					2nd cut	0	37/20	0.10/0.20	
						1	0.55/0.96	<0.05/<0.05	
						4	0.05/0.26	<0.05/<0.05	
					3rd cut	0	54/7.7	0.13/0.06	
						1	11/6.5	<0.05/0.08	
						4	0.73/0.06	<0.05/<0.05	

State Year	Application Form	No.	kg ai/ha		Sample analysed	PHI, days	Residue, mg/kg Malathion	Malaoxon	Reference
	ULV aerial	2	0.68		Forage/hay	0	9.0/5.6	<0.05/<0.05	
					1st cut	1	0.07/0.42	<0.05/<0.05	
						4	0.07/0.14	<0.05/<0.05	
					2nd cut	0	9.7/6.2	<0.05/<0.05	
						1	0.27/0.24	<0.05/<0.05	
						4	0.18/<0.05	<0.05/<0.05	
					3rd cut	0	8.7/2.1	<0.05/<0.05	
						1	3.2/3.1	<0.05/<0.05	
						4	0.70/0.05	<0.05/<0.05	
MN 1993	EC	2	1.4		Forage/hay	0	35/	0.06	MN1
					1st cut	1	1.0/	<0.05	
						4	0.20/	<0.05	
					2nd cut	0	29/2.0	0.06/<0.05	
						1	20/3.1	<0.05/<0.05	
						4	0.96/1.1	<0.05/<0.05	
	ULV aerial	2	0.47-0.68		Forage/hay	0	5.7/8.6	<0.05/<0.05	
					1st cut	1	5.5/3.3	<0.05/<0.05	
						4	3.8/2.3	<0.05/<0.05	
					2nd cut	0	21/9.7	<0.05/<0.05	
						1	2.2/8.5	<0.05/<0.05	
						4	2.0/0.43	<0.05/<0.05	
NE 1993	EC	2	1.4		Forage/hay	0	23/	<0.05	NE1
					1st cut	1	11/	<0.05	
						4	0.33/	<0.05	
					2nd cut	0	45/20	0.08/0.16	
						1	2.5/1.8	<0.05/<0.05	
						4	0.57/0.57	<0.05/<0.05	
					3rd cut	0	28/1.5	0.09/<0.05	
						1	5.4/0.20	<0.05/<0.05	
						4	0.41/0.29	<0.05/<0.05	
	ULV aerial	2	0.68		Forage/hay	0	17/19	<0.05/<0.05	
					1st cut	1	15/7.7	<0.05/<0.05	
						4	0.79/1.7	<0.05/<0.05	
					2nd cut	0	32/38	<0.05/0.08	
						1	11/13	<0.05/<0.05	
						4	2.6/7.0	<0.05/<0.05	
					3rd cut	0	22/4.6	0.06/<0.05	
						1	9.4/1.9	<0.05/<0.05	
						4	1.7/1.8	<0.05/<0.05	
PA 1993	EC	2	1.4		Forage/hay	0	98/46	0.11/0.27	PA1
					1st cut	1	53/33	0.16/0.25	
						4	4.7/5.5	0.13/0.15	
					2nd cut	0	19/3.9	0.06/<0.05	
						1	0.98/1.6	<0.05/<0.05	
						4	0.27/0.57	<0.05<0.05	
					3rd cut	0	65/3.2	0.09/<0.05	
						1	19/3.1	<0.05/<0.05	
						4	0.94/0.10	<0.05/<0.05	
	ULV aerial	2	0.68		Forage/hay	0	22/33	<0.05/0.10	
					1st cut	1	20/24	0.06/0.12	
						4	5.3/6.8	<0.05/<0.05	
					2nd cut	0	10/21	<0.05/<0.05	
						1	10/10	<0.05/<0.05	
						4	7.1/11	<0.05/<0.05	
					3rd cut	0	19/26	<0.05/0.05	
						1	38/20	0.06/<0.05	
						4	14/8.7	<0.05/<0.05	
SD 1992	EC	2	1.4		Forage/hay	0	47/11	0.13/0.08	SD1
					1st cut	1	2.0/0.89	<0.05/<0.05	
						4	0.33/0.28	<0.05/<0.05	
						7	0.07/0.22	<0.05/<0.05	
						14	0.07/<0.05	<0.05/<0.05	

State Year	Application Form	No.	kg ai/ha		Sample analysed	PHI, days	Residue, mg/kg Malathion	Malaoxon	Reference
	ULV aerial	2	0.54-0.71		Forage/hay 1st cut	0	1.8/3.5	<0.05/<0.05	
						1	0.30/0.43	<0.05/<0.05	
						4	0.09/0.23	<0.05/<0.05	
						7	<0.05/0.05	<0.05/<0.05	
						14	<0.05/0.08	<0.05/<0.05	
1993	EC	2	1.4		Forage/hay 1st cut	0	70/175	0.15/2.1	SD1A
						1	31/64	0.10/0.87	
						4	4.0/5.8	<0.05/0.10	
	ULV aerial	2	0.68		Forage/hay 1st cut	0	29/135	<0.05/0.43	
						1	18/81	<0.05/0.35	
						4	/37	/0.09	
WA 1993	EC	2	1.4		Forage/hay 1st cut	0	22/16	<0.05/0.10	WA1
						1	1.7/3.7	0.07/0.07	
					2nd cut	0	68/28	0.07/0.27	
						1	11/5.7	<0.05/<0.05	
						4	0.24/0.85	<0.05/<0.05	
					3rd cut	0	81/6.7	0.10/0.05	
						1	12/1.8	<0.05/<0.05	
						4	0.20/0.26	<0.05/<0.05	
	ULV aerial	2	0.68		Forage/hay 1st cut	0	0.99/2.8	<0.05/<0.05	
						1	0.27/0.44	<0.05/<0.05	
					2nd cut	0	4.5/2.9	<0.05/<0.05	
						1	0.84/0.22	<0.05/<0.05	
						4	<0.05/0.06	<0.05/<0.05	
					3rd cut	0	12/2.1	<0.05/<0.05	
						1	0.33/0.10	<0.05/<0.05	
						4	0.06/<0.05	<0.05/<0.05	
WI 1992	EC	2	1.4		Forage/hay 1st cut	0	42/52	0.05/0.33	WI1
						1	12/17	<0.05/0.09	
						4	0.89/3.4	<0.05/<0.05	
						7	0.54/2.6	<0.05/<0.05	
						14	0.16/0.27	<0.05/<0.05	
					2nd cut	0	32/85	<0.05/0.59	
						1	46/83	<0.05/0.54	
						4	6.6/6.7	<0.05/0.07	
						7	1.4/	<0.05	
						14	0.32/	<0.05	
	ULV aerial	2	0.68		Forage/hay 1st cut	0	5.2/3.3	<0.05/<0.05	
						1	2.1/1.6	<0.05/<0.05	
						4	1.6/0.47	<0.05/<0.05	
						7	1.0/0.32	<0.05/<0.05	
						14	1.0/0.08	<0.05/<0.05	
					2nd cut	0	21/45	<0.05/0.21	
						1	22/46	<0.05/0.24	
						4	18/13	<0.05/0.05	
						7	6.8/	<0.05	
						14	1.5/	<0.05	

Grasses. In twenty trials on various grasses with ground EC or air ULV application malathion residues at the allowed 0 day PHI varied from 2.0 to 190 mg/kg in forage and from 1.9 to 260 mg/kg in hay (Table 68).

Table 68**.** Residues of malathion and oxon in grasses at 0 day PHI (Study No. AA920113).

State Year	Application Form	No.	kg ai/ha		Sample	Residue, mg/kg Malathion	Malaoxon
AR 1993	EC	3	1.4		Forage	25	0.23
					Hay	6.0	0.08
	ULV aerial	2	1.0		Forage	80	0.07
					Hay	30	0.14

State Year	Application				Sample	Residue, mg/kg	
	Form	No.	kg ai/ha			Malathion	Malaoxon
KS 1992	EC	3	1.4		Forage	72	<0.05
					Hay	4.0	<0.05
	ULV aerial	2	1.0		Forage	83	<0.05
					Hay	34	<0.05
KY 1993	EC	3	1.4		Forage	2.0	<0.05
					Hay	1.9	<0.05
	ULV aerial	2	1.0		Forage	19	<0.05
					Hay	33	<0.05
MO 1993	EC	3	1.4		Forage	68	0.06
					Hay	58	0.19
	ULV aerial	2	1.0		Forage	68	<0.05
					Hay	55	0.16
NY 1993	EC	3	1.4		Forage	29	0.06
					Hay	24	0.34
	ULV aerial	2	1.0		Forage	10	<0.05
					Hay	68	0.34
OK 1992	EC	3	1.4		Forage	22	0.05
					Hay	42	0.15
	ULV aerial	2	1.0		Forage	44	<0.05
					Hay	54	<0.05
PA 1993	EC	3	1.4		Forage	130	0.06
					Hay	260	0.80
	ULV aerial	2	1.0		Forage	190	0.16
					Hay	130	0.70
SD 1993	EC	3	1.4		Forage	55	0.06
					Hay	36	0.12
	ULV aerial	2	1.0		Forage	74	0.06
					Hay	46	0.08
TN 1993	EC	3	1.4		Forage	34	0.18
					Hay	61	0.52
	ULV aerial	2	1.0		Forage	30	<0.05
					Hay	100	0.34
VA 1993	EC	3	1.4		Forage	75	0.05
					Hay	66	0.73
	ULV aerial	2	1.0		Forage	38	<0.05
					Hay	27	0.07

FATE OF RESIDUES IN PROCESSING

All the processing studies were in the USA and simulated commercial procedures.

Oranges. In a processing study in California, malathion was applied at 8 times the label rate (1.75 kg ai/ha) and oranges were harvested after 7 days. Samples of whole oranges, oil, juice, peel, dried pulp and molasses were analysed. Malathion was concentrated in oil (factor 219), dried pulp (factor 10) and molasses (factor 1.4) (Table 69).

Table 69. Malathion residues in oranges and their processed products.

Sample	Residues, mg/kg		Processing factor	
	Malathion	Malaoxon	Malathion	Malaoxon
Orange	0.18	<0.01	-	-
Oil	40	0.04	219	4
Juice	<0.01	<0.01	<0.05	-
Peel	0.10	<0.01	0.55	-
Dried pulp	1.8	<0.05	10	-
Molasses	0.26	<0.01	1.4	-

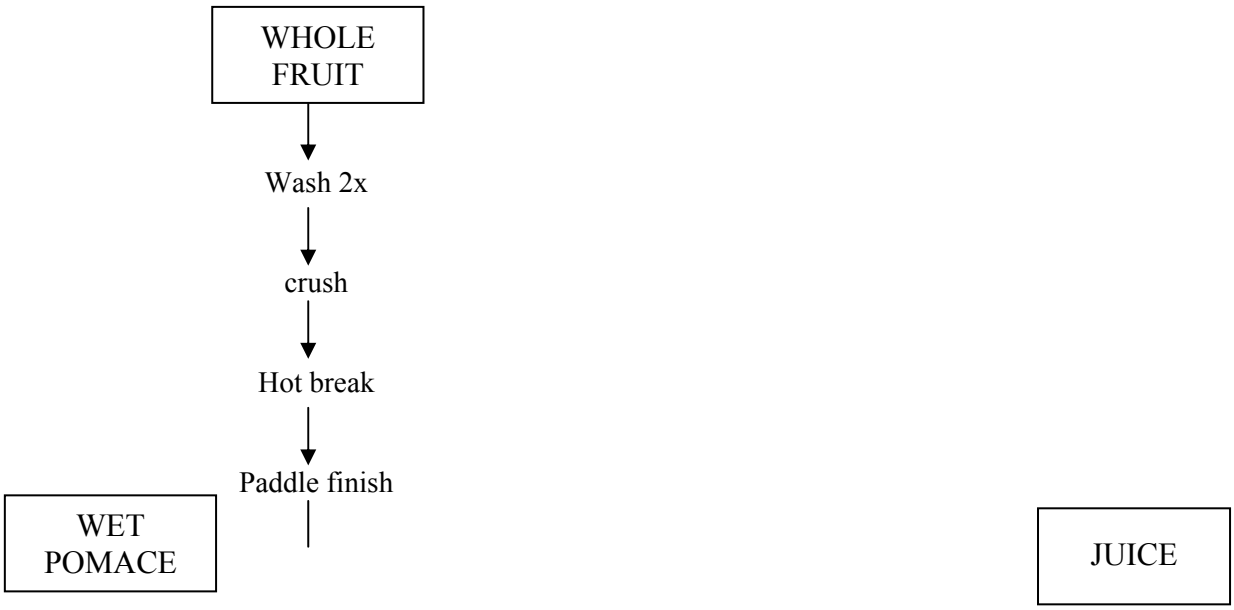
Grapes. In a processing study in California, malathion was applied twice at 10.5 kg ai/ha (5 times the label rate) and grapes were harvested 3 days after the last application. Malathion was concentrated in wet pomace (factor 2.5), dry pomace (factor 11) and raisin waste (factor 6) (Table 70).

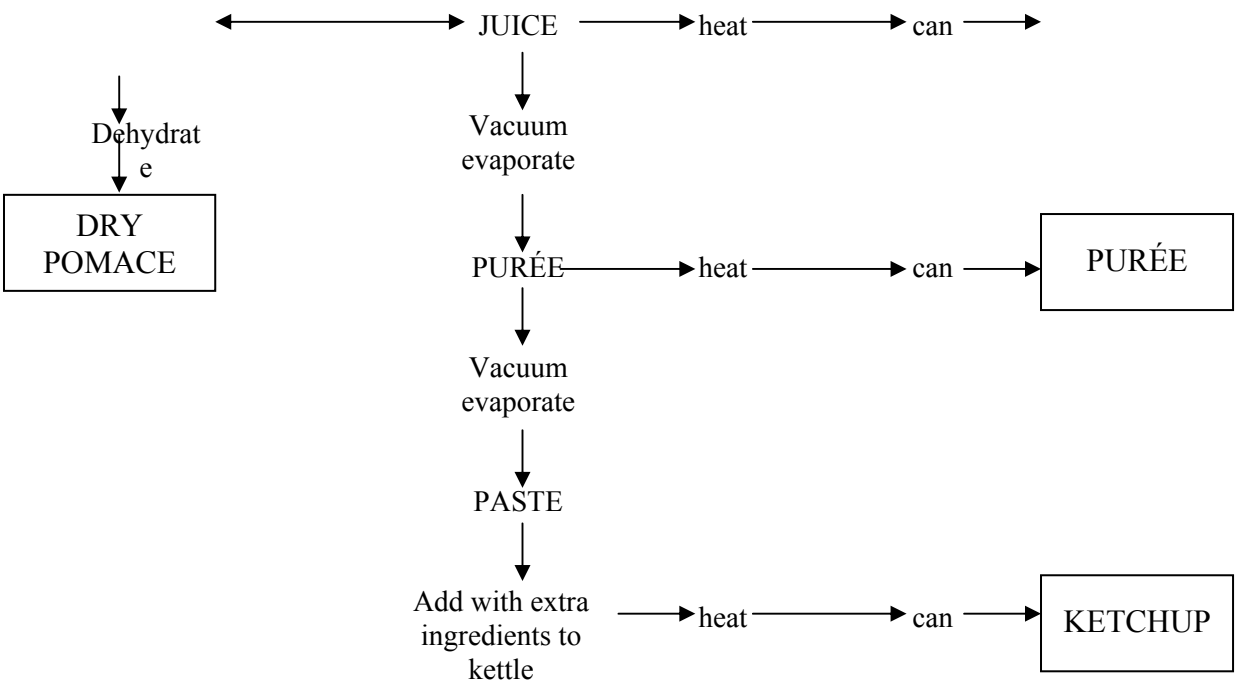
Table 70. Malathion residues in grapes and their processed products.

Sample	Residue, mg/kg		Processing factor	
	Malathion	Malaoxon	Malathion	Malaoxon
Whole grapes	0.79	0.04	-	-
Juice	0.07	0.01	0.08	0.25
Wet pomace	2.0	0.07	2.5	1.8
Dry pomace	8.8	0.18	11	4.5
Raisins	0.34	0.02	0.43	0.5
Raisin waste	4.9	0.48	6	12

Tomatoes. In a processing study in California, malathion was applied at 5 x 19.2 kg ai/ha (5 times the maximum label rate) and tomatoes harvested 1 day after the last application were processed according to a simulated commercial procedure. The fruit were flume-spray washed twice, crushed, heated to 91.1°C, and passed through a 0.83 mm screen. The portion that did not pass through the screen (wet pomace) was dried and a sub-sample of the juice that passed through the screen was heated in a steam-jacketed kettle to >65.6°C and canned. The cans were sealed and heated for at least 50 minutes at ≥115.6°C. Another sub-sample of the juice was concentrated by vacuum evaporation to produce purée. A sub-sample of the purée was heated to 90°C and canned. Another sub-sample of the purée was vacuum-condensed to paste and mixed with other ingredients to produce ketchup, heated to 92.2°C in a steam-jacketed kettle and canned. The procedure is shown in Figure 5.

Figure 5. Flow chart of tomato processing procedure.





Malathion residues were concentrated in wet pomace by a factor of 1.7 and dry pomace by a factor of 13.3 (Table 71).

Table 71. Malathion residues in processed tomatoes and processed fractions.

	Residue, mg/kg		Processing factor	
Sample	Malathion	Malaoxon	Malathion	Malaoxon
Tomato	24	0.17	-	-
Juice	0.69	<0.01	0.03	<0.06
Purée	14	0.10	0.58	0.59
Ketchup	18	0.14	0.75	0.82
Dry pomace	320	2.5	13.3	14.7
Wet pomace	41	0.23	1.7	1.4

Snap beans. In a processing study in Oregon malathion was applied at 3 x 3.4 kg ai/ha (5 times the maximum label rate) and beans were harvested 1 day after the last application. The beans were washed in water, the debris, stems and blossom ends were removed, and the beans mechanically cut. The removed parts were analysed as cannery waste, in which malathion was concentrated 8.3 times (Table 72).

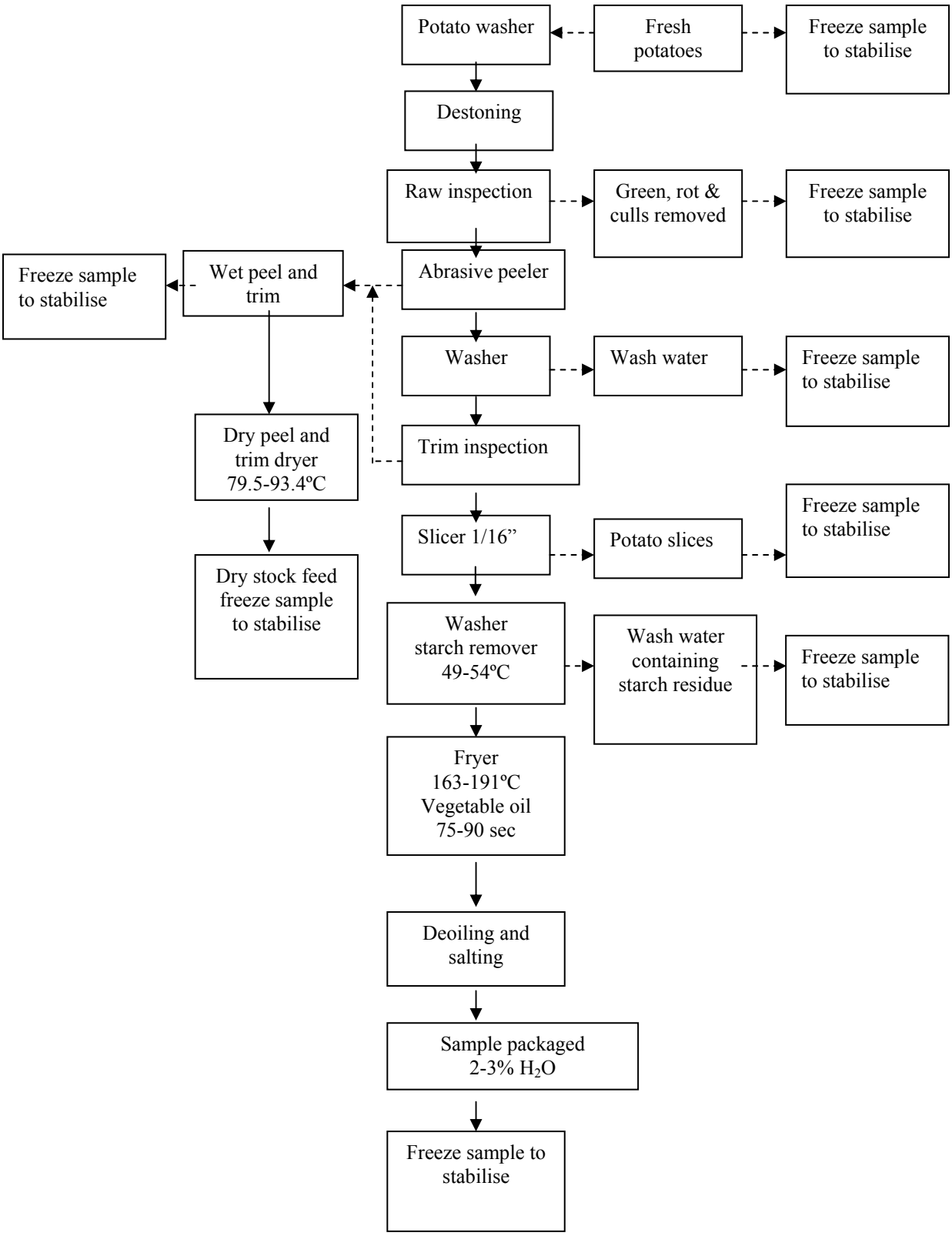
Table 72. Malathion residues in snap beans and processed fractions.

Samples	Residue, mg/kg		Processing factor	
	Malathion	Malaoxon	Malathion	Malaoxon
Whole bean	0.55	<0.01	-	-
Cut bean	<0.01	<0.01	<0.02	-
Cannery waste	4.6	<0.05	8.3	-

Potatoes. In a processing study in Washington malathion was applied at 2 x 8.7 kg ai/ha (5 times the maximum label rate) and potatoes were harvested on the day of the last application. Tubers were processed according to a simulated commercial procedure. Potatoes were tub-washed, batch-peeled, hand-trimmed to remove damaged areas, sliced, fried at 160 to 167.7°C, drained, salted and packaged as potato chips. The remaining washed raw potatoes were steam-peeled, mechanically scrubbed, hand-trimmed to removed damaged portions and the wet peel was hydraulically pressed. The pressed peel was mixed with the cut trim waste and a sample collected and packaged as the wet peel fraction. The remaining wet peel was air-dried, milled, and a sample packaged as the dry peel fraction. A sub-sample of raw peeled tubers was sliced, spray-washed with water to remove free starch, pre-cooked at 67.8 to 73.9°C in a stainless steel steam-jacketed kettle and cooled to <32.2°C. A sub-sample of the cooled potato slices was steam-cooked at 99.4°C, mashed in a commercial meat grinder, mixed with reweighed food additives, dried to 10% moisture in a fluid-bed drier, sifted through a US 30-mesh screen, air-cooled to 8-10% moisture and passed through a US 60-mesh screen. The material passing through the screen was packaged as potato granules. The procedure is shown in Figure 6.

Samples of whole potato tubers, granules, dry peel, wet peel and chips were analysed. The residue level was <0.01 mg/kg in the whole potato tubers. Malathion residues were detected only in dry peel at a level of 0.06 mg/kg.

Figure 6. Potato processing.



Maize. In a processing study in Texas, malathion was applied at 3 x 7 kg ai/ha (5 times the maximum label rate) and the grain harvested 7 days after the last application. Samples of whole grain, grain dust, grits, meal, flour, crude and refined oil (dry milling and wet milling), B&D oil (dry milling and wet milling) and starch were analysed. Residues of malathion were detected only in grain dust (Table 73).

In a post-harvest trial on maize, the storage bin was treated with 2.4 kg ai/hl of an EC formulation and the grain received 3 applications of a dust formulation during and after bin loading and storage for 59 days. Residues in the processed fractions are shown in Table 73.

Table 73**.** Residues of malathion in maize and processed fractions.

Treatment	Sample analysed	Residues, mg/kg		Processing factor	
		Malathion	Malaoxon	Malathion	Malaoxon
Pre-harvest (Study AA920312)	Grain	<0.01	<0.01	-	-
	Aspirated grain fraction (>2540 µm)	0.99	<0.05	99	-
	Aspirated grain fraction (≤2540 µm)	0.74	<0.05	74	-
Post-harvest (Study No. 41702)	Grain	6.9	0.03	-	-
	Aspirated grain fraction (>2540 µm)	1170	17	170	567
	Aspirated grain fraction (≤2540 µm)	670	7.5	97	250
	Grits	5.2	0.05	0.75	1.7
	Meal	12	0.09	1.7	3
	Flour	14	0.12	2.0	4
	Dry-milled crude oil	31	0.10	4.5	3.3
	Dry-milled refined oil	9.5	<0.01	1.4	<0.33
	Dry milled bleached/deodorized oil	0.11	<0.01	0.016	<0.33
	Wet-milled starch	0.02	<0.01	0.002	<0.33
	Wet-milled crude oil	43	0.10	6.2	3.3
	Wet-milled refined oil	24	<0.01	3.5	<0.33
	Wet-milled bleached/deodorized oil	0.15	<0.01	0.02	<0.33

Rice. In a processing study in Louisiana, malathion was applied at 3 x 7 kg ai/ha (5 times the maximum rate) and grains were harvested 7 days after the last application. Residues of malathion were concentrated by factors of 1.7 in grain dust >2540 µm, 2.5 in dust <2540 µm, and 5.5 in hulls (Table 74).

Table 74. Residues of malathion in rice and processed fractions (Report No. AA9200137).

Sample	Residues, mg/kg		Processing factor	
	Malathion	Malaoxon	Malathion	Malaoxon
Grain	24	0.52	-	-
Polished rice	0.54	<0.01	0.02	<0.02
Hulls	135	2.5	5.5	4.8
Bran	16	0.22	0.67	0.42
Grain dust ≥ 2540	42	0.83	1.7	1.6
Grain dust <2540	62	1.5	2.5	2.9

Wheat. In a processing study in Kansas, malathion was applied at 3 x 7 kg ai/ha (5 times the maximum label rate) and grain was harvested 7 days after the last application. Residues of malathion were concentrated in grain dust by factors of 36 in dust >2540 µm and 56 in dust <2540 µm, and by 2.2 in middlings. In another study with post-harvest treatment, the storage bin was treated with 2.4 kg ai/hl of an EC formulation and the grain with 3 applications of a dust formulation during and after bin loading and after 59 days of storage. Residues were concentrated in the aspired grain fraction, with processing factors of 1.25 and 35 for dust >2540 µm and ≤2540 µm respectively (Table 75).

Table 75. Residues of malathion in wheat and processed fractions.

Sample	Residues, mg/kg		Processing factor	
	Malathion	Malaoxon	Malathion	Malaoxon
Grain (pre-harvest) (Report No. AA9200136)	1.5	0.02	-	-
Bran	0.61	<0.01	0.41	<0.5
Middlings	3.3	0.03	2.2	1.5
Shorts (>240μm)	0.59	<0.01	0.39	<0.5
Patent flour (<132 μm)	0.35	<0.01	0.23	<0.5
Grain dust ≥ 2540	54	0.76	36	38
Grain dust <2540	84	1.2	56	60
Grain (post-harvest) (Report No. 41701)	8.0	<0.01	-	-
Aspirated grain fraction (>2540 μm)	10	<0.05	1.25	-
Aspirated grain fraction (≤2540 μm)	283	0.56	35	56

Cotton. In a processing study in Mississippi, malathion was applied at 25 x 14 kg ai/ha (3.3 times the maximum label rate) and cotton seed was harvested at the day of the last application. Residues of malathion were not concentrated in any of the fractions analysed (Table 76).

Table 76. Residues of malathion in cotton and processed cotton (Report No. AA9200131)

Sample	Residues, mg/kg		Processing factor	
	Malathion	Malaoxon	Malathion	Malaoxon
Seed	330	0.69	-	-
Hulls	255	0.86	0.77	1.24
Meals	23	0.15	0.07	0.22
Crude oil	220	0.30	0.67	0.43
Refined oil	215	0.03	0.65	0.04
Bleached and deodorized oil	2.5	<0.01	0.008	<0.014

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Government of Australia submitted monitoring data from a market basket survey study in 1996 and target enforcement monitoring studies from 1996 to 1998. In the survey study malathion was detected in psyllium husk (maximum 0.02 mg/kg), silverbeet (maximum 0.50 mg/kg) and strawberries (maximum 0.10 mg/kg). In enforcement monitoring, 289 samples of fruits, grain and vegetables were analysed (LOD 0.02 and 0.05 mg/kg). Malathion was detected at half the MRL in one celery sample.

In monitoring by The Netherlands from 1994 to 1996 analysed 19828 samples of 31 fruits, vegetables and cereals. Twelve percent of the samples had detectable residues, with a mean of <0.02 mg/kg.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Country	Commodity	MRLs, mg/kg
Australia Residue definition: malathion	Wheat bran unprocessed	20
	Beans, lentil, dry, cereal grains, dried fruits, grapes, peanut, tree nuts	8
	Citrus fruits	4
	Kale, tomato	3
	Fruits (except blueberries, citrus fruits, dried fruits, grapes, pear, strawberry), other vegetables	2
	Mammalian edible offal, mammalian, meat fat, eggs, milk fat, poultry fat meat, poultry edible offal, strawberry,	1
	Blueberries, cauliflower, chard (silver beet), egg plant, garden pea, kohlrabi, pear,	0.5

Country	Commodity	MRLs, mg/kg
	peppers, sweet (capsicums), root and tuber vegetables, turnip, garden, chard	
The Netherlands	Bran	20
Residue definition:	Dried fruit, pulses, cereals	8
malathion, including	Other vegetables	3
malaoxon, expressed as	Citrus fruit, whole meal	2
malathion	Other fruit, root and tuber vegetables	0.5
	Tea	0.1
	Other food commodities	0.02
Poland	Cereals grains	8
	Citrus fruit	2
	Fruits except citrus fruits, vegetables	0.5
	Tea	0.1

APPRAISAL

Malathion is an insecticide and acaricide which was originally scheduled for periodic re-evaluation by the 1995 JMPR. The review was postponed by the 1994 CCPR and re-scheduled for periodic re-evaluation of residue aspects in 1999. The manufacturer provided residue data, information on GAP and studies to support existing CXLs. Other data on use patterns, methods of residue analysis, residues in food in commerce or at consumption and national residue limits were provided by the governments of Australia, The Netherlands, Thailand, Poland and the UK.

Metabolism

Studies of metabolism in animals and plants were with [^{14}C]malathion labelled at the 2 and 3 position of the succinate moiety.

In laying hens dosed with the equivalent of 25 ppm in the feed for 4 days, malathion was metabolised within 24 hours. The highest concentration of radioactivity was in the faeces, with a total radioactive residue (TRR) of 14 mg/kg as malathion at day 2. In the egg yolks radioactivity was detected by the fourth day, with a TRR of 0.96 mg/kg. In egg whites the TRR was 0.33 mg/kg on days 1 and 4. The highest concentration of radioactivity in the tissues was in the kidneys and liver (1.08 and 0.77 mg/kg respectively) and the lowest levels were in light and dark muscle (0.11 mg/kg). No malathion or any products of immediate metabolism exceeded 0.05 mg/kg in any of the samples except the white from one egg (day 1), where significant activity from malathion carboxylic acid was detected. This result, however, was attributed to contamination by faeces, which had been shown to contain the metabolite. Incorporation of ^{14}C was found in carboxylic acids, proteins and triglycerides. The extensive metabolism of malathion in hens results in low residues in the eggs and tissues.

In goats dosed with the equivalent of 115 ppm malathion in the diet for five days, the highest concentration of radioactivity was found at day 5, with fat, kidney and liver samples showing 1.42-2.23 as malathion. The TRR in heart and muscle samples ranged from 0.26 to 0.39 mg/kg. Radioactivity in the milk increased from 1.42 mg/kg at day 1 to 2.46 mg/kg at day 4 then decreased to 2.14 mg/kg on day 5. In the kidneys, the monocarboxylic acid was detected at 0.06 mg/kg. No malathion or any immediate metabolites were observed at levels above 0.05 mg/kg in any other sample analysed. [^{14}C]Malathion was found to be a carbon source for the production of triglycerides, which were incorporated in the tricarboxylic acid cycle and lactose. The extensive metabolism of malathion in goats again results in low residues in the milk and tissues

Metabolism studies on rats evaluated by the 1997 JMPR also showed that malathion was rapidly absorbed, biotransformed and excreted within 24 h. Most of the administered dose was recovered in the urine (76-90% of the TRR) and faeces (6.6-14%), with below 1% in the tissues. The main metabolites were malathion monocarboxylic and dicarboxylic acids .

Plant metabolism studies on cotton, wheat, alfalfa and lettuce showed that the metabolism of malathion in plants proceeds via malathion dicarboxylic acid to succinic acid which is incorporated into plant constituents such as starch, proteins, pectin, lignin, hemicellulose and cellulose.

Cotton plants were treated at 1.46 kg ai/ha and leaves and mature and immature bolls collected approximately 18 h after the last application. The TRR in immature bolls, lint and gin trash was 55.6, 217 and 428 mg/kg malathion equivalents respectively. The main component identified in organic solvent extracts of the seed was malathion, representing 33% of the total radioactive residue (49.4 mg/kg). Malathion monocarboxylic acid and malaoxon were at 2.6% and 0.2% of the total radioactivity in the residue respectively. Polar extracts contained 12.9% of the TRR of which 9.6% was characterized, with succinate the main component (2.0% of the TRR). Approximately 67% of the radioactivity was recovered in the experiment.

In wheat plants treated three times at 1.68-1.8 kg ai/ha, malathion was the main component of the organic solvent extracts, representing 13%, 27% and 11% of the TRR in forage, grain and straw respectively. Malathion monocarboxylic acid (6% of the TRR in forage 0.5% in grain, 7.3% in straw) and malathion dicarboxylic acid (4.9% of the TRR in forage, 1.1% in grain and 0.1% in straw) were the main metabolites. Malaoxon was present at low levels (<0.01-0.4% of the TRR). From 82 to 89% of the radioactivity was recovered from each wheat fraction.

When alfalfa plants were treated twice with malathion at 2.0-2.1 kg ai/ha, samples harvested 18 h after the last application contained malathion as the main residue (42% of the TRR in forage and 16.4% in hay), followed by malathion monocarboxylic acid (9.8% and 2.7% in forage and hay) and malaoxon (0.8% of the TRR in hay). More than 80% of the radioactivity was recovered in the experiment.

Malathion was applied at 6 x 2.0 kg ai/ha to lettuce and the plants were harvested 14 days after the last treatment. Malathion represented 36.8%, malathion monocarboxylic acid 12.8% and malaoxon 1.2% of the total radioactivity in the residue. Aqueous extracts contained 44% of the TRR and organic extracts 58% of the TRR.

In summary, the metabolism of malathion in animals and plants is qualitatively similar. Malathion is hydrolysed to mono and dicarboxylic acids and these metabolites are further degraded and incorporated into animal and plant constituents. A major quantitative difference is that no parent compound or primary metabolite was detected in animal tissues, eggs or milk, whereas in plants malathion was the main residue with up to 12.8% of the TRR representing its monocarboxylic acid metabolite.

Environmental fate

All the studies were with malathion labelled at the 2 and 3 positions of the succinate moiety.

Adsorption/desorption

Malathion was adsorbed in moderate amounts by sandy loam, sand, loam and silt loam soils with K_d varying from 0.83 to 2.47 and K_{oc} from 151 to 308. Adsorption generally increased as soil organic matter, clay content and cation exchange capacity increased. The ß-substituted monocarboxilic acid was the main degradation product representing 0.1 to 8.6% of the TRR in adsorption solutions and 0.3 to 9% of the TRR in desorption solutions. The experiment lasted approximately 3 h and the samples

were flushed with nitrogen initially. Malathion was fairly stable under the experimental conditions, accounting for 74.2 to 98.6% of the TRR.

When [^{14}C]malathion was applied to 2 non-sterile soils at 6.88-8.86 mg/kg dry weight kept in the dark at 22 °C, the half life was 4.9 h. After 1 day malathion represented on average 2.6% of the TRR. The main extractable product was malathion dicarboxylic acid (13.8 and 1.1% of the TRR after 6 h and 4 days respectively). Bound residues and $^{14}CO_2$ represented >50% of the TRR at day 7. Dissipation of ^{14}C residues by volatilization was insignificant. No degradation of malathion was observed after 4 days in the sterile control sample.

A study of aerobic and anaerobic degradation of malathion on a loamy sand soil was conducted at 25°C in the dark. The main degradation products in both systems were malathion dicarboxylic acid (up to 62.3% of the TRR on day 7 under aerobic conditions), $^{14}CO_2$, and bound residues. Malathion was degraded with a half-life of 1 day under aerobic conditions and <30 days under anaerobic conditions.

The dissipation of malathion was studied in bare soil and in a cotton field after six applications at 1.13 kg ai/ha. No residues were found below a 30 cm depth in the crop plot or below 15 cm in the bare ground plot. Malathion was not detected in any soil samples later than one day after the last application (up to 0.14 mg/kg dry weight). Malathion dicarboxylic acid was detected in only two samples (at 0.11 mg/kg in bare soil one day after the last application and at 0.016 mg/kg in the cotton plot after the second application). No malaoxon was detected in any sample analysed (<0.01 mg/kg).

Photodegradation does not appear to be a major mechanism of degradation of malathion. In a study with sandy loam fortified on the surface with 10 mg/kg [^{14}C]malathion and kept at 25°C under a 12-hour light/12-hour dark cycle over a 30-day period, the rate constant and extrapolated half-life of malathion were 0.00399 day^{-1} and 173 days respectively. A shorter half-life of 63.5 days found in the control sample (24 h dark) is believed to be a result of increased microbial activity.

The leaching potential of [^{14}C]malathion and its degradation products was evaluated in 4 types of soil aged for approximately one half-life (14.3, 2.1, 0.5 and 0.9 h for sand, sandy loam, loam and silty clay respectively). Two flasks of each soil were sampled after dosing, two at the ageing period and two mixed thoroughly and added to the top of replicate columns containing untreated soil of each type. Five to 74.4% of the radioactivity was found in the leachate. Malathion was found to leach only from the sand column (1.9% of the TRR). The dicarboxylic acid was the main compound, with up to 47.5% of the TRR in the leachates, followed by the monocarboxylic acid (0.1 to 13.3% of the TRR).

The volatility of malathion was evaluated in a silt loam soil spiked with the “Ready to use”, ULV and EC formulations at the recommended field rate, with air flows of 100 and 300 ml/min and 50% and 75% soil field capacity. Volatile ^{14}C was found only with the EC formulation (50% soil moisture and 100 ml/min), where 26.5% of the applied dose was recovered as CO_2.

The aquatic degradation of malathion in a water/sediment system fortified with 1.108-1.02 mg/kg was evaluated under aerobic and anaerobic conditions at 22°C in the dark. The two monocarboxylic acids, demethyl-monocarboxylic acids, dicarboxylic acid and demethyl-dicarboxylic acid were mainly associated with the water, with maximum concentrations from 20.9 to 46.4% of the TRR. In the sediment the concentrations ranged from 3.6 to 8.1%. Dissipation by volatilization was minimal, with <0.5 and <0.1% of the TRR in aerobic and anaerobic conditions respectively. Half-lives of malathion in water and sediment in aerobic conditions were 1.09 and 2.55 days respectively and in anaerobic conditions 2.49 and 2.45 days.

Analytical methods for malathion and malaoxon in plants and processed commodities were submitted by the manufacturer. The analytes are extracted with acetonitrile and acetonitrile/water (80:20), the organic extract is cleaned up on activated carbon and silica gel extraction cartridges and the analytes are quantified by gas chromatography with a flame photometric detector in the phosphorus mode. Recoveries of malathion and malaoxon averaged 89.6% and 98.2% respectively. The LOD is 0.01 mg/kg for all raw and processed human food analysed and 0.05 mg/kg for raw and processed animal feed. For dry samples a hydration step is included before the extraction. Lipids are removed from the extracts with hexanes and the analytes are partitioned 3 times with dichloromethane.

In a multi-residue method reported by The Netherlands for non-fatty samples, no clean-up is necessary and the analytes are determined by GLC with an NPD or ion-trap detector. The LOD for both malathion and malaoxon is 0.02 mg/kg. In an Australian method for organophosphorus insecticides, clean-up was by gel-permeation chromatography and dialysis from a semi-permeable membrane followed by alumina column. The analytes are determined by GLC with an NPD or FPD with an LOD of 0.01 and 0.02 mg/kg.

The stability of residues in stored analytical samples was determined in various raw and processed agricultural commodities. Duplicate samples were fortified with 0.50 mg/kg malathion and malaoxon and stored at <-5°C for 12 months. The analytes were stable for 12 months, with 69 to 105% of malathion and 91 to 109% of malaoxon remaining at the end of the study.

Definition of the residue

In plants, malathion was the main residue. The highest metabolite concentration (monocarboxylic acid) was 13% of the labelled residue. This metabolite is rapidly metabolized further in animals. The Meeting agreed that the residue should be defined as malathion *per se* for compliance with MRLs and for the estimation of dietary intake.

Residues resulting from supervised trials

All the trials were in the USA during the years 1990 to 1997.

Oranges. In six trials in California and Florida with ground applications of EC formulations below the maximum GAP for citrus (28.4 kg ai/ha), residues of malathion at 7 days PHI varied from 0.42 to 1.9 mg/kg. Eight other trials with ULV formulations with aerial and ground application at the proposed or higher rates gave residues ranging from <0.01 to 2.9 mg/kg.

As no data from trials at the maximum GAP rate were reported the Meeting could not recommend an MRL for oranges and as no data were reported for other citrus fruits, the Meeting recommended withdrawal of the existing MRL.

Apples. In three trials in Tennessee, California and Michigan below the maximum GAP rate (20 kg ai/ha), residues at 3 days PHI varied from 0.05 to 2.6 mg/kg. Three other trials at shorter PHIs or higher rates showed residues ranging from 0.19 to 2.5 mg/kg and as no data from trials at the maximum GAP rate were reported, the Meeting recommended withdrawal of the existing MRL.

Pears. In three trials below maximum GAP rate (20 kg ai/ha) in California, New York and Washington, residues at a PHI of 1 day were 0.34 to 1.9 mg/kg. As there were no trials at the maximum GAP rate, the Meeting recommended withdrawal of the existing MRL for pears.

Cherries. In one trial on sweet cherries in California with ground application at maximum GAP (10 kg ai/ha, 3 days PHI), the residues were 1.8 mg/kg. Other trials with ground application at a lower rate gave residues ranging from 0.26 to 2.6 mg/kg. In another six trials in California, Oregon, Michigan, Montana and New York with aerial ULV application at the GAP rate (1.0-1.3 kg ai/ha, 1-day PHI), the residues were 0.02, 0.03, 0.08, 0.17, 0.34 and 0.47 mg/kg.

It is clear that ground application gives higher residues than aerial application, even when the application rate is not the maximum allowed by GAP.

The Meeting concluded that insufficient data from trials with ground application at the maximum GAP rate had been reported and recommended withdrawal of the existing MRL for cherries.

Apricots and peaches. In one trial on apricots and four on peaches in New Jersey, Michigan, California and Georgia with 4-5 applications of 4.2 kg ai/ha, residues after 6 or 7 days varied from 0.16 to 1.4 mg/kg. GAP rate for these commodities is 1.6 to 12 kg ai/ha. As no data from trials at the maximum GAP rate were reported, the Meeting could not recommend an MRL for apricot and recommended withdrawal of the existing MRL for peaches.

Grapes. In six trials in California, Washington and New York at 2.1 kg ai/ha (the GAP rate is 2.3-3.1 kg ai/ha), residues at a PHI of 3 days ranged from 0.33 to 2.7 mg/kg. As no data from trials at the maximum GAP rate were reported, the Meeting recommended withdrawal of the existing MRL for grapes.

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Strawberries. In seven trials in Pennsylvania, Oregon, California and Florida with EC or WP formulations within the range of EC GAP rates (1.2-2.7 kg ai/ha), residues at 3 days PHI were 0.09, 0.16, 0.19, 0.25, 0.39, 0.53 and 0.59 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg, the same as the previous MRL, and an STMR of 0.25 mg/kg for strawberries.

Blueberries. In seven trials in Michigan, Oregon and Maine, with ground applications of EC formulations at 0.75 and 1.4 kg ai/ha (GAP 1.7-2.8 kg ai/ha), residues at a 1-day PHI varied from 0.26 to 7.1 mg/kg. In another four trials with aerial applications of a ULV formulation close to the GAP rate (0.8 kg ai/ha) residues at a 0-day PHI were 0.06, 0.55, 4.0 and 7.5 mg/kg.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 2.27 mg/kg for blueberry.

Blackberries and raspberries. In six trials in California and Oregon on blackberries and four in Washington on raspberries with WP and EC formulations within the EC GAP range at 2.1-2.27 kg ai/ha (GAP is 1.3-4.6 kg ai/ha), residues at 1 day varied from 1.3 to 11 mg/kg.

As no data from trials at the maximum GAP rate were reported, the Meeting recommended withdrawal of the existing MRLs for blackberries and raspberries.

Avocado. In two trials in California at 5.3 kg ai/ha (GAP rate is 5.4-12 kg ai/ha), residues were 0.07 and 0.08 mg/kg at 7 days PHI. As no data from trials at the maximum GAP rate were reported, the Meeting could not estimate a maximum residue level for avocado.

Figs. In two trials in California within the GAP range (2.7–3.3 kg ai/ha) samples harvested at a longer PHI than the proposed GAP interval contained malathion residues of 0.32 and 0.36 mg/kg. As no trials were conducted according to GAP, the Meeting could not estimate a maximum residue level or an STMR.

Guavas. Three trials in Hawaii and Florida were at a higher rate than the proposed GAP (1.0 kg ai/ha, 2 days PHI). Malathion residues 1 or 2 days after the last application were 0.10, 0.24 and 0.30 mg/kg. As no trials were according to GAP, the Meeting could not estimate a maximum residue level or an STMR.

Mangoes and sugar apples. In one trial on each in Florida at the proposed GAP rate for mangoes (1.4-11.2 kg ai/ha) the residues were 0.31 mg/kg at 3 days and 0.07 mg/kg at 1 day. As no trials were according to approved GAP, the Meeting could not estimate a maximum residue level or an STMR.

Papayas. In three trials in Hawaii and Florida according to the proposed GAP (1.4-14 kg ai/ha), malathion residues (PHI 1 day) ranged from <0.05 to 0.56 mg/kg. As no trials were according to approved GAP, the Meeting could not estimate a maximum residue level.

Onions. In six trials on bulb onions and six on green onions in California, Oregon, New York, Texas and Nebraska within the GAP range (1.2-2.4 kg ai/ha), residues of malathion at 3 days PHI were 0.02, 0.08, 0.11, 0.35, 0.37 and 0.59 mg/kg in bulb onions and 0.18, 0.19, 0.35, 0.69, 2.5, 5.0 mg/kg in green onions.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.23 mg/kg for bulb onions and a maximum residue level of 5 mg/kg and an STMR of 0.52 mg/kg for green onions,

Broccoli. In five trials in New York, Tennessee, Washington and California at 1.4 kg ai/ha (GAP is 0.1-3.4 kg ai/ha)), the residues at 3-5 days PHI varied from 0.02 to 9.3 mg/kg. As no trials were at the maximum GAP rate, the Meeting recommended withdrawal of the existing MRL for broccoli.

Cabbage. In fourteen trials on head cabbages in Wisconsin, Ohio, New York, Florida, Washington, California, Indiana and Texas at 1.4 kg ai/ha (GAP is 0.1-3.4 kg ai/ha), samples with or without the wrapper leaves at 7 days PHI had malathion residues of <0.05 (13) and 0.10 mg/kg. As no trials were at the maximum GAP rate, the Meeting could not estimate a maximum residue level.

Cucumbers. Nine trials were conducted in Florida, New Jersey, Texas, North Carolina, California and Michigan. GAP allows up to 1.6 kg ai/ha with PHI of 1 day and up to 2.3 kg ai/ha with PHI of 3 days. Trials carried out at 2.1 kg ai/ha gave residues at a PHI of 1 day of <0.01, 0.01, 0.02 (3), 0.03 (2), 0.06 and 0.10 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.02 mg/kg.

Cantaloupes and watermelons. In two trials on cantaloupes and one trial on watermelons in Georgia, California and Texas at 6 x 1.12 kg ai/ha (GAP for melons is 1.2-2.3 kg ai/ha), residues at a 1-day PHI were <0.05 (2) and 0.80 mg/kg. As there were so few trials and none was at maximum GAP, the Meeting could not estimate a maximum residue level or STMR.

Mushrooms. In one trial in Pennsylvania at the GAP rate of 4 x 1.9 kg ai/ha, malathion residues were <0.05 mg/kg at a PHI of 1 day. There were insufficient data from trials according to GAP to estimate a maximum residue level or an STMR.

Peppers. In seven trials in New Jersey, Florida, North Carolina, California, Michigan and Texas close to maximum GAP (2.0 kg ai/ha), malathion residues at 3 days PHI were ≤0.01 (4), 0.02, 0.05 and 0.08 mg/kg. The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.01 mg/kg.

Tomatoes. The maximum GAP for tomatoes in the USA is 2.3 kg ai/ha with a PHI of 1 day and up to 4.9 kg ai/ha with a PHI of 5 days. In seven trials in New Jersey, Florida, Michigan and California at 1.74 kg ai/ha, malathion residues at a 1 day PHI were 0.10, 0.14, 0.17, 0.21, 0.27, 0.33 and 0.41

mg/kg. In seven other trials at 3.84 kg ai/ha, residues varied from 0.13 to 1.2 mg/kg 3 days after application. These trials did not comply with GAP and were not used for evaluation.

The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.21 mg/kg.

Sweet corn. In six trials in Wisconsin, Washington, Montana, California, Florida and New York with ground applications of an EC formulation close to the maximum GAP rate (1.6 kg ai/ha) residues in the kernels + cobs at 5 days PHI were <0.01 (5) and 0.02 mg/kg. In six trials with aerial application of a ULV formulation the residues were <0.01 mg/kg. There is no approved use of aerial application on sweet corn in the USA.

The Meeting estimated a maximum residue level of 0.02 mg/kg and an STMR of 0.01 mg/kg for sweet corn (grain).

The residues in the forage from the 12 trials were also determined. Those from the ground applications are evaluated with the residues in field corn (maize) forage.

Okra. In two trials in South Carolina and Texas within the GAP range (1.2-2.0 kg ai/ha), malathion residues at a 1-day PHI were <0.05 and 2.1 mg/kg.

There were insufficient data to estimate a maximum residue level or an STMR.

Lettuce. In two trials in California on leaf lettuce according to GAP (1.6-2.7 kg ai/ha), the residues at a PHI of 14 days were 0.99 and 3.1 mg/kg. In four other trials at the same rate in New Jersey, Florida, Washington and Arizona, wrapper leaves were removed from the samples before analysis. In 3 trials in California on head lettuce at the same rate, residues ranged from 0.01 to 0.17 mg/kg after 14 days.

The Meeting concluded that there were insufficient data from trials according to GAP to estimate a maximum residue level for leaf lettuce. As there were no trails according to GAP on head lettuce the Meeting recommended withdrawal of the existing MRL.

Mustard greens. In seven trials in South Carolina, North Carolina, Indiana, Washington, California, Georgia, Texas and Arizona according to GAP (0.8-1.6 kg ai/ha), malathion residues at 7 days PHI were <0.05 (2), 0.07 (2), 0.46, 0.52 and 1.1 mg/kg. In seven other trials conducted at nearly twice the higher GAP rate the residues ranged from <0.05 to 5.9 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.07 mg/kg.

Spinach. In five trials in New Jersey, Texas, South Carolina, Washington and California within the GAP range (1.3-2.7 kg ai/ha.), malathion residues at a PHI of 7 days were <0.05, 0.16, 0.35, 1.1 and 2.2 mg/kg. One trial under the same conditions gave a residue of 36 mg/kg. As all the other residues in spinach and other leafy vegetables were in a much lower range, this value was not considered for estimation.

The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.35 mg/kg.

Watercress. In three trials in Florida and Hawaii at 0.5 and 1.4 kg ai/ha (GAP is 1.3-2.7 kg ai/ha), residues of malathion were <0.05 mg/kg in samples taken after 7 days. As there were no trials at maximum GAP, the Meeting could not estimate a maximum residue level.

Beans. Five trials were conducted on lima beans in Wisconsin, Florida, Pennsylvania, North Carolina and California, and five on snap beans in Wisconsin, Oregon and New York with aerial applications according to GAP (0.7 kg ai/ha). At a PHI of 1 day, the residues were <0.01, 0.05, 0.12, 0.13, 0.21, 0.41, 0.49, 0.56, 0.71 and 0.90 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.31 mg/kg for beans, except broad beans and soya beans. The Meeting also recommended withdrawal of the existing MRL of 2 mg/kg for common beans.

Peas. In two trials in California and Wisconsin close to the maximum GAP rate (3.3 kg ai/ha) malathion residues at 3 days were 0.38 and 0.96 mg/kg in peas with pods and 2.9 and 32 mg/kg in dry forage. One other trial gave residues of 0.34 mg/kg in peas with pods 2 days after the last application.

The Meeting concluded that there were too few trials according to GAP and recommended withdrawal of the existing MRL.

Beans, dry. In ten trials in Michigan, California, Idaho, New York and Nebraska with aerial applications according to GAP (0.7 kg ai/ha), malathion residues at 1 day were 0.07, 0.10 (2), 0.16, 0.36, 0.39, 0.42, 0.62 and 1.2 mg/kg.

The Meeting noted that the existing MRL was based on post-harvest treatment and estimated a maximum residue level of 2 mg/kg and an STMR of 0.36 mg/g for dry beans.

Potatoes. In fifteen trials in Idaho, Maine, Florida, Wisconsin and Nebraska at 2 x 1.74 kg ai/ha (GAP is 0.8-3.3 kg ai/ha), malathion residues at day 0 were <0.01(14) and 0.02 mg/kg. As no data from trials at the maximum GAP rate were reported, the Meeting could not recommended a maximum residue level.

Turnips. In six trials in Georgia, Indiana, Ohio, California, South Carolina, Washington and Texas near the maximum GAP rate (1.6 kg ai/ha), malathion residues in the tops at 7 days were <0.05 (2), 0.99, 1.4, 1.8 and 3.4 mg/kg, and in the roots ≤0.05 (4), 0.09 and 0.13 mg/kg. In one trial at the higher rate, residues in the tops were 15 and 10 mg/kg and in the roots 0.11 mg/kg.

The Meeting estimated a maximum residue level of 0.2 mg/kg and an STMR of 0.05 mg/kg for turnip roots, and a maximum residue level of 5 mg/kg and an STMR of 1.195 mg/kg for turnip tops.

Carrots. In six trials in Wisconsin, New Jersey, Florida, Washington, California and Texas at 1.4 kg ai/ha (GAP is 1.2-2.4 kg ai/ha) residues ranged from <0.05 to 0.54 mg/kg after 7 days. As no data from trials at the maximum GAP rate were reported, the Meeting could not estimate a maximum residue level.

Celery. In two trials in Florida and California within the GAP range (1.2-2.0 kg ai/ha), residues at 7 days were 0.91 and 1.2 mg/kg. There were insufficient data from trials according to GAP reported and the Meeting recommended withdrawal of the existing MRL.

Asparagus. In four trials in California, New Jersey, Washington and Wisconsin close to maximum GAP (1.7 kg ai/ha), residues at 1 day were 0.10, 0.13, 0.48 and 0.69 mg/kg.

The Meeting estimated a maximum residue level of 1 mg/kg and an STMR of 0.305 mg/kg.

Wheat. Twenty trials were conducted in Oklahoma, Kansas, Ohio, Washington, North Dakota and Montana on winter and spring wheat according to GAP with either ground application of an EC formulation (GAP is 1.2-1.7 kg ai/ha) or aerial application of a ULV formulation (GAP is 0.3-0.7 kg ai/ha). The residues at a PHI of 7 days in grain from the trials with ground applications were <0.01, 0.02, 0.03, 0.04 (3), 0.08, 0.10 and 0.14 mg/kg and from trials with aerial applications <0.01 (2), 0.03, 0.04 (2), 0.08, 0.09, 0.10, 0.20, 0.22 and 0.28 mg/kg. The residues from the two applications

constitute a single population with residues of <0.01 (3), 0.02, 0.03 (2), 0.04 (5), 0.08 (2), 0.09, 0.10(2), 0.14, 0.20, 0.22 and 0.28 mg/kg.

In a single trial with post-harvest application of dust formulation according to GAP, the residue in the grain after 59 days of storage was 7.5 mg/kg. This trial was not considered in the estimation as one trial in not enough to reflect residues from post-harvest applications.

The Meeting estimated a maximum residue level of 0.5 mg/kg and an STMR of 0.04 mg/kg for wheat grain.

In forage the residues on a fresh weight basis from ground applications were <0.05 (9) and 0.09 mg/kg and from aerial application <0.05, 0.19, 0.23, 0.27, 0.49, 1.3, 1.8, 1.9, 2.3 and 2.4 mg/kg. The two residue populations are distinct so the higher residues from the aerial applications were used for estimation. The range of the moisture contents of the analysed samples was stated to be 70-85%, with a mean of 78.4%. Applying this value to the median and highest residues from aerial application (0.895 and 2.4 mg/kg respectively) gives values on a dry weight basis of 4.14 and 11 mg/kg.

The Meeting estimated a maximum residue level of 20 mg/kg and an STMR of 4.14 mg/kg for wheat forage.

In straw the residues from ground applications were <0.05, 0.66, 0.68, 0.81, 1.6, 2.2, 2.5, 3.2, 3.8 and 9.4 mg/kg, and from aerial applications 1.0, 1.4, 3.2, 5.1, 6.5, 7.2, 8.4, 12, 18 and 34 mg/kg. As in forage, the residues in straw were higher from ground applications and were used for estimation. The Meeting estimated a maximum residue level of 50 mg/kg and an STMR of 6.85 mg/kg for wheat straw (fodder).

Sorghum. In four trials in Texas and Nebraska with ground applications of EC formulations close to the GAP rate (1.2 kg ai/ha) the residues in the grain at 7 days PHI were 0.02, 0.07, 0.12 and 0.49 mg/kg. In four other trials with aerial applications of a ULV formulation according to GAP (0.7-1.0 kg ai/ha) residues were 0.13, 0.34, 2.0 and 2.2 mg/kg at 7 days. The residues from both modes of application, considered to be a single population, were 0.02, 0.07, 0.12, 0.13, 0.34, 0.49, 2.0 and 2.2 mg/kg.

The Meeting estimated a maximum residue level of 3 mg/kg and an STMR of 0.235 mg/kg for sorghum (grain).

Maize. Twenty one trials on field corn in Indiana, Illinois, Nebraska, Ohio, Texas and Wisconsin at GAP rate were with either ground applications of EC formulations (GAP is 1.2-1.6 kg ai/ha, 5 days PHI) or aerial applications of ULV formulations (GAP is 0.266-0.533 kg ai/ha, 5 days PHI). In the grain the residues 7 days after the last application from the ground trials were <0.01 (5), 0.01, 0.02 (3) mg/kg and from the aerial trials <0.01 (11) and 0.02 mg/kg. The residues from both applications form a single population with the rank order ≤0.01 (16), 0.01, 0.02 (4) mg/kg.

In a post-harvest trial according to GAP the residue in the grain after 60 days of storage was 6.9 mg/kg. This trial was not considered in the estimation as one result is not enough to reflect residues from post-harvest applications.

The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg for maize (grain).

The residues in the forage from the ground applications were <0.05 (7), 0.12 and 0.19 mg/kg and from the aerial applications <0.05, 0.06, 0.07, 0.09 (2), 0.15, 0.24, 0.34, 0.22, 0.25, 0.76 and 1.2 mg/kg. The residues in the sweet corn forage from ground applications according to GAP were <0.05 (2), 0.20, 0.33, 1.7 and 2.4 mg/kg. The three populations can be combined, giving residues in rank

order of <0.05 (10), 0.06, 0.07, 0.09 (2), 0.12, 0.15, 0.19, 0.20, 0.22, 0.24, 0.25, 0.33, 0.34, 0.76, 1.2, 1.7 and 2.4 mg/kg. Applying a moisture content of 56% (specified for sweet corn and corn forage in the FAO Manual) to the median and the highest residues in the three populations (0.09 and 2.4 mg/kg respectively) gives values on a dry weight basis of 0.20 and 5.4 mg/kg respectively.

The Meeting estimated a maximum residue level of 10 mg/kg and an STMR of 0.20 mg/kg for maize forage.

In straw, the residues from ground applications were 1.3, 1.8, 2.3, 3.2, 3.4, 4.5, 4.6, 4.7, 11 and 13 mg/kg and from aerial applications 1.4, 5.0, 6.6, 6.7, 6.9, 8.0, 11, 12 (2), 19, 22, 24 mg/kg. The two applications give the single population of residues in rank order 1.3, 1.4, 1.8, 2.3, 3.2, 3.4, 4.5, 4.6, 4.7, 5.0, 6.6, 6.7, 6.9, 8.0, 11 (2), 12 (2), 13, 19, 22 and 24 mg/kg.

The Meeting estimated a maximum residue level of 50 mg/kg and an STMR of 6.65 mg/kg for maize fodder.

Nuts. In two trials in Florida on chestnuts close to the maximum GAP rate (6.8 kg ai/ha), the residues at 2 days were 0.08 and 0.58 mg/kg. In two trials on macadamia nuts in Hawaii far below maximum GAP rate (16.7 kg ai/ha) the residues were <0.05 mg/kg at 1 day. In two trials on walnuts in California near the maximum GAP rate (3.14 kg ai/ha), no residues were detected at 7 days. For the three uses on nuts the labels state that application may be at the time of harvest.

As the data from trials at the maximum GAP rate were limited, the Meeting could not estimate a maximum residue level for malathion in chestnuts, macadamia nuts or walnuts, and recommended the withdrawal of the existing MRL for tree nuts.

Cotton. Seventeen trials were conducted in Texas, Arizona, California and Louisiana according to GAP with either ground applications of EC formulations (GAP is 0.4-3.14 kg ai/ha) or air applications of ULV and Ready-to-use formulations (ULV GAP is 0.3-1.4 kg ai/ha). The residues in the cotton seed at a 0-day PHI from EC formulations were 3.0, 3.8, 4.1, 7.1, 7.8 and 14 mg/kg, and from Ready-to-use formulations 2.3, 4.2, 4.3, 4.8, 4.9 and 5.4 mg/kg and from ULV formulations 2.1, 2.7, 5.4, 5.9 and 6.4 mg/kg. The residues from the three formulations, which constitute a single population, were 2.1, 2.3, 2.7, 3.0, 3.8, 4.1, 4.2, 4.7, 4.8, 4.9, 5.4 (2), 5.9, 6.4, 7.1, 7.8 and 14 mg/kg.

The Meeting estimated a maximum residue level of 20 mg/kg and an STMR of 4.8 mg/kg for cotton seed.

Flax. In one trial in Nevada at a proposed GAP rate of 1 x 0.56 kg ai/ha, no residues were found in samples of straw, seed or meal after 52 days (the LOD is 0.05 mg/kg). There were insufficient data to estimate a maximum residue level or an STMR for flax.

Mint. In three trials on peppermint and spearmint in Wisconsin and Idaho below the maximum GAP rate (1.6 kg ai/ha), the residues in fresh mint at a PHI of 7 days were 0.51, 1.2 and 1.4 mg/kg and in mint oil 5.7, 8.0 and 9.1 mg/kg. In four trials at about 3 times the maximum GAP the residues were 13-56 mg/kg in fresh mint and 140-460 mg/kg in oil.

As there were no trials at the maximum GAP rate, the Meeting could not estimate a maximum residue level for mint.

Clover. Twenty six trials were conducted in Wisconsin, Michigan, Idaho, Oklahoma, Georgia, New York and Minnesota with either ground application of an EC formulation at 1.4 kg ai/ha (GAP is 1.2-1.6 kg ai/ha) or aerial application of a ULV formulation at 0.68 kg ai/ha (GAP is 0.7-1.0 kg ai/ha). Two applications were made before each cutting (up to 3 cuts) and each cut was considered to be one trial. Samples were taken after 0 to 14 days (GAP allows application at harvest).

The residues in the forage at day 0 from trials with the EC formulation were 14, 17, 18, 31, 20, 37, 39, 40, 57, 71, 73, 88 and 95 mg/kg, and from trials with the ULV formulation 2.8, 3.2, 8.7, 9.5, 14, 16, 25, 33, 38, 39, 46, 56 and 60 mg/kg. The residues from the two modes of application constitute one population with residues of 2.8, 3.2, 8.7, 9.5, 14 (2), 16, 17, 18, 20, 25, 31, 33, 37, 38, 39 (2), 40, 46, 56, 57, 60, 71, 73, 88 and 95 mg/kg. The range of moisture contents of the analysed sample was stated to be 71-85%, with a mean of 81%. Applying this value to the median and highest residues (32 and 95 mg/kg respectively) gives values on a dry weight basis of 168 and 500 mg/kg.

The Meeting estimated a maximum residue level of 500 mg/kg and an STMR of 168 mg/kg for clover forage.

In hay, the residues from foliar applications were 9.2, 9.7, 16, 21, 34, 35, 36, 53, 64, 86 90 and 120 mg/kg, and from aerial applications 4.4, 5.0, 12, 15, 18, 19, 20, 26, 33, 49, 58, 90, 93 and 98 mg/kg. These formed a single population with residues of 4.4, 5.0, 9.2, 9.7, 12, 15, 16, 18, 19, 20, 21, 26, 33, 34, 35, 36, 49, 53, 58, 64, 86, 90 (2), 93, 98 and 120 mg/kg.

The Meeting estimated a maximum residue level of 150 mg/kg and an STMR of 33.5 mg/kg for clover hay.

Alfalfa. Two series of eleven trials each were conducted in Pennsylvania, Wisconsin, Michigan, South Dakota, Iowa, Washington, California, Minnesota, Idaho and Nebraska either with ground application of 1.4 kg ai/ha of an EC formulation (GAP is 1.2-1.96 kg ai/ha) or aerial application of 0.68 kg ai/ha of an ULV formulation (GAP is 0.5-1.1 kg ai/ha). Two applications were made before each cutting (up to 3 cuts) and samples were taken after 0 to 14 days (GAP allows application at harvest).

Malathion residues in forage at day 0 from trials with the EC formulation were 19, 22, 23, 28, 29, 34, 35, 37, 40, 42, 45, 45, 47, 51 (2), 53, 54, 60, 64, 65, 68, 70, 81, 92, 95 and 98 mg/kg, and from aerial application 0.99, 1.8, 4.5, 5.2, 5.7, 8.7, 9.0, 9.7, 10, 12, 17, 20, 21, 22, (3), 23, 25, 29, 32, 36, 38, 41, 43, 72 and 95 mg/kg, forming a single population with residues of 0.99, 1.8, 4.5, 5.2, 5.7, 8.7, 9.0, 9.7, 10, 12, 17, 19, 20, 21, 22 (4), 23 (2), 25, 28, 29 (2), 32, 34, 35, 36, 37, 38, 40, 41, 42, 43, 45, 46, 47, 51 (2), 53, 54, 60, 64, 65, 68, 70, 72, 81, 92, 95 (2) and 98 mg/kg. The Meeting was informed that the moisture contents of the forage samples varied from 71-85%, with a mean of 78%. This value was used to calculate the median and highest residues in forage on a dry weight basis: 157 and 445 mg/kg.

The Meeting estimated a maximum residue level of 500 mg/kg and an STMR of 157 mg/kg for alfalfa forage (dry weight).

In hay, the residues at day 0 after EC treatment were 1.5, 2.0, 3.2, 3.9, 6.1, 6.5, 7.7, 11, 16, 17 (2), 20 (2), 27, 43, 46, 52, 85, 140 and 175 mg/kg and after aerial treatment 2.1 (2), 2.8, 2.9, 3.3, 3.5, 4.4, 4.6, 5.6, 6.2, 8.6, 9.7, 12, 14, 19, 20, 21, 25, 26 (2), 33, 38, 45, 52, 56, 67 and 135 mg/kg, forming a single population with residues of 1.5, 2.0, 2.1 (2), 2.8, 2.9, 3.2, 3.3, 3.5, 3.9, 4.4, 4.6, 5.6, 6.1, 6.2, 6.5, 7.7, 8.6, 9.7, 11, 12, 14, 16, 17 (2), 19, 20 (3), 21, 25, 26 (2), 33, 38, 43, 45, 46, 52 (2), 56, 67, 85, 135, 140 and 175 mg/kg.

The Meeting estimated a maximum residue level of 200 mg/kg and an STMR of 17 mg/kg for alfalfa fodder (hay).

Grasses. Twenty trials in Montana, Virginia, Oklahoma, South Dakota, Kansas, Tennessee, Arkansas, Pennsylvania, Kentucky and New York were with either ground application of an EC formulation (GAP is 1.2-1.6 kg ai/ha) or aerial application of a ULV formulation (GAP is 0.5-0.8 kg ai/ha). The residues at day 0 (GAP allows application at harvest) in grass forage were 2.0, 19, 10, 22, 25, 29, 30,

34, 38, 44, 55, 68 (2), 72, 74, 75, 80, 83, 130 and 190 mg/kg and in hay 1.9, 4.0, 6.0, 24, 27, 30, 33, 34, 36, 42, 46, 54, 55, 58, 61, 66, 68, 100, 130 and 260 mg/kg.

The Meeting estimated a maximum residue level of 200 mg/kg and an STMR of 49.5 mg/kg for grass forage and a maximum residue level of 300 mg/kg and an STMR of 44 mg/kg for grass hay.

Fate of residues in processing

In a processing study on oranges, malathion was applied at 8 times the label rate and oranges were harvested 7 days after the last application. Malathion was concentrated in oil (processing factor 219), dried pulp (processing factor 10) and molasses (processing factor 1.4). The residues in the juice were decreased considerably (processing factor <0.05).

In a processing study with grapes, malathion was applied at 5 times the label rate and grapes were harvested 3 days after the last application. Malathion was concentrated in wet pomace (processing factor 2.5), dry pomace (processing factor 11) and raisin waste (processing factor 6). The residues in juice and raisins were decreased considerably with processing factors of 0.08 and 0.43 respectively.

Tomatoes were treated with malathion at 5 times the maximum label rate and harvested 1 day after the last application. Malathion residues were concentrated in the wet pomace (processing factor 1.7) and dry pomace (processing factor 13.3), and decreased in juice, purée and ketchup with processing factors of 0.03, 0.58 and 0.75 respectively.

In a processing study on snap beans in Oregon, malathion was applied at 5 times the maximum label rate and beans were harvested 1 day after the last application. The beans were washed in water, the debris, stems and blossom ends were removed and the beans mechanically cut to give cut beans. Residues were concentrated in the removed parts (cannery waste) with a processing factor of 8.3, and residues in cut beans decreased considerably with a processing factor of<0.02.

Potatoes were treated at 5 times the maximum label rate and harvested on the day of the last application. Residues in whole potato tubers, granules, wet peel and chips were <0.01 mg/kg. Malathion was detected only in the dry peel at a level of 0.06 mg/kg.

Malathion was applied at 5 times the maximum label rate to field corn and the grain harvested 7 days after the last application. Whole grain, grain dust, grits, meal, flour, crude and refined oil (dry milling and wet milling), bleached and deodorised oil (dry milling and wet milling) and starch were analysed. Malathion was detected only in grain dust at levels of 0.99 and 0.74 mg/kg in dust >2540 μm and ≤2540 μm respectively.

In a post-harvest trial according to GAP, the residues were concentrated in the aspirated grain by processing factors (PF) of 170 and 97 in >2540 μm and ≤2540 μm fractions respectively, meal (PF = 1.7), flour (PF 2.0), dry milled crude oil (PF 4.5), dry milled refined oil (PF 1.4), wet milled crude oil (PF 6.2) and wet milled refined oil (PF 3.5). The residues were decreased in grits, dry and wet milled bleached/deodorized oil and wet milled starch, by processing factors of 0.7, 0.016, 0.02 and 0.002 respectively. The Meeting concluded however that it was unlikely that malathion would be concentrated in flour, and agreed not to estimate a maximum residue level for maize flour.

In a processing study on rice, malathion was applied at 5 times the maximum rate and grain was harvested 7 days after the last application. The residues were concentrated in grain dust (PF 1.7 in dust >2540 μm and 2.5 in dust <2540 μm) and in hulls (PF 5.5). The residues were decreased in polished rice and bran by processing factors of 0.02 and 0.67 respectively. The Meeting concluded that it was unlikely that malathion would be decreased after processing to bran.

In a processing study on wheat, malathion was applied at 5 times the maximum label rate and grain was harvested 7 days after the last application. Malathion residues were concentrated after processing in grain dust, with a factor of 36 in dust >2540 μm and of 56 in dust ≤ 2540 μm and in middlings (between 240 and 730 μm) with a processing factor of 2.2. In bran, shorts (>240 μm) and patent flour (<132 μm), residues were reduced with processing factors of 0.41, 0.39 and 0.23 respectively. The Meeting concluded however that it was unlikely that malathion residue in wheat would be decreased after processing to bran. In another study with post-harvest treatment conducted according to GAP, residues in grain were concentrated in the aspirated grain fraction, with PF 1.25 and 35 for dust >2540 μm and ≤2540 μm respectively.

In a processing study on cotton, malathion was applied at 3.3 times the maximum label rate and cotton seed was harvested on the day of the last application. The residues of malathion decreased in all fractions analysed, with processing factors of 0.77 in hull, 0.07 in meal, 0.67 in crude oil, 0.65 in refined oil and 0.008 in bleached and deodorized oil.

Residues in food in commerce or at consumption

Monitoring by the governments of Australia and The Netherlands from 1994 to 1998 showed that malathion residues were undetectable (LOD 0.02 and 0.05 mg/kg) in most of the samples of fruit, grain and vegetables analysed. In a market survey in Australia malathion was detected only in psyllium husk (maximum 0.02 mg/kg), silver beet (maximum 0.50 mg/kg) and strawberries (maximum 0.10 mg/kg). In enforcement monitoring of 289 samples, malathion was detected only in one celery sample. In monitoring in The Netherlands from 1994 to 1996 12% of the 19828 samples analysed had detectable residues, with a mean of <0.02 mg/kg.

RECOMMENDATIONS

On the basis of data from supervised residue trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for the estimation of dietary intake: malathion.

Commodity		Recommended MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
AL 1020	Alfalfa fodder	200		17
AL 1021	Alfalfa forage (green)	500 dry wt.		157 dry wt.
FP 0226	Apple	W	2	
VS 0621	Asparagus	1		0.305
VP 0071	Beans (dry)	2	8 Po	0.36
VP 0061	Beans, except Broad bean and Soya bean	1		0.31
FB 0264	Blackberries	W	8	
FB 0020	Blueberries	10	0.5	2.27
VB 0400	Broccoli	W	5	
VB 0041	Cabbages, Head	W	8	
VB 0404	Cauliflower	W	0.5	
VS 0624	Celery	W	1	
GC 0080	Cereal grains	W	8 Po	
VL 0464	Chard	W	0.5	
FS 0013	Cherries	W	6	
FC 0001	Citrus fruits	W	4	
AL 1023	Clover	500 dry wt.		168 dry wt.
AL 1031	Clover hay or fodder	150		33.5

Commodity		Recommended MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
VP 0526	Common bean (pods and/or immature seeds)	W	2	
SO 0691	Cotton seed	20		4.8
	Cotton seed meal			0.34
	Cotton seed oil, blanched and deodorized			0.038
OC 0691	Cotton seed oil, crude	13		3.21
OR 0691	Cotton seed oil, edible	13		3.12
VC 0424	Cucumber	0.2		0.02
DF 0167	Dried fruits	W	8	
VO 0440	Egg plant	W	0.5	
VL 0476	Endive	W	8	
FB 0269	Grapes	W	8	
AF 0162	Grass forage	200		49.5
AS 0162	Hay or fodder (dry) of grasses	300		44
VL 0480	Kale	W	3	
VB 0405	Kohlrabi	W	0.5	
VD 0533	Lentil (dry)	W	8	
VL 0482	Lettuce, Head	W	8	
GC 0645	Maize	0.05		0.01
AS 0645	Maize fodder	50		6.65
AF 0645	Maize forage	10 dry wt.		0.20 dry wt.
VL 0485	Mustard greens	2		0.07
	Nuts (whole in shell)	W	8	
VA 0385	Onion, Bulb	1		0.23
FS 0247	Peach	W	6	
FP 0230	Pear	W	0.5	
VP 0063	Peas (pods and succulent = immature seeds)	W	0.5	
VO 0051	Peppers	0.1	0.5	0.01
FS 0014	Plums (including Prunes)	W	6	
FB 0272	Raspberries, Red, Black	W	8	
VR 0075	Root and tuber vegetables [1]	W	0.5	
CM 0650	Rye bran, unprocessed	W	20 PoP	
CF 1250	Rye flour	W	2 PoP	
CF 1251	Rye wholemeal	W	2 PoP	
GC 0651	Sorghum	3		0.235
VL 0502	Spinach	3	8	0.35
VA 0389	Spring onion	5		0.52
FB 0275	Strawberry	1	1	0.25
VO 0447	Sweet corn (corn-on the-cob)	0.02		0.01
VO 0448	Tomato	0.5	3	0.21
JF 0448	Tomato juice	0.01		0.00
	Tomato ketchup			0.09
	Tomato pomace, wet			0.20
	Tomato pomace, dry			1.6
	Tomato purée			0.07
VR 0506	Turnip, Garden	0.2	3	0.05
VL 0506	Turnip greens	5		1.20
GC 0654	Wheat	0.5		0.04
AF 0654	Wheat forage	20 dry wt.		4.14 dry wt.
AS 0654	Wheat straw and fodder, dry	50		6.85

[1] Except Turnip, Garden

FURTHER WORK OR INFORMATION

Desirable

1. Farm animal feeding studies.

2. Processing studies on wheat, rice and maize (corn) treated pre-harvest.

DIETARY RISK ASSESSMENT

Chronic intake

Thirty six STMRs were estimated for malathion. There were consumption data for 20 commodities which were used with the STMRs for the dietary intake calculation. The results are shown in Annex III.

International Estimated Daily Intakes for the five GEMS/Food regional diets, based on estimated STMRs, were 0% of the ADI. The Meeting concluded that the intake of residues of malathion resulting from its uses that have been considered by the JMPR is unlikely to present a public heath concern.

Acute intake

The international estimate of short-term intake (IESTI) for malathion was calculated for the commodities for which maximum residue levels and STMRs were estimated and for which consumption data (large portion consumption, unit weight) were available. The results are shown in Annex IV. The IESTI varied from 0 to 0.017 mg/kg body weight in the general population and from 0 to 0.058 mg/kg body weight in children. As no acute reference dose has been established, the acute risk assessment for malathion was not finalized.

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METHIOCARB (132)

EXPLANATION

Methiocarb, or mercaptodimethur, an insecticide, acaricide, molluscicide, and bird repellent was identified by the 1995 CCPR as a candidate for periodic review (ALINORM 95/24A, Annex 1). It was scheduled for toxicological and residue reviews by the 1998 and 1999 JMPR respectively (ALINORM 97/24A, Appendix III). The most recent extensive reviews of methiocarb residue chemistry were in 1981 and 1983.

The manufacturer is Bayer AG.

IDENTITY

ISO common name: methiocarb
mercaptodimethur

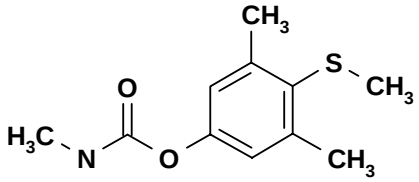
Chemical names:
IUPAC: 4-methylthio-3,5xylyl methylcarbamate
CA: 3,5-dimethyl-4-(methylthio)phenyl methylcarbamate

CAS Number: 2032-65-7

CIPAC Number: 165

Synonyms: BAY 37344
Mesurol

Structural formula:



Molecular formula: $C_{11}H_{15}NO_2S$

Molecular weight: 225.3

Physical and chemical properties

Pure active ingredient

Vapour pressure: 0.015 mPa at 20°C
0.036 mPa at 25°C

Melting point: 119°C

Octanol/water partition Coefficient:	log P_{ow} = 3.11 at 20°C and pH 4 log P_{ow} = 3.18 at 20°C and pH 7 degradation at pH 9 log P_{ow} = 3.08 at 20°C unbuffered (Krohn, 1995)
Solubility:	0.027 g/l at 20°C in water (Krohn, 1989) 1.3 g/l at 20°C in n-hexane 33 g/l at 20°C in toluene >200 g/l at 20°C in dichloromethane 53 g/l at 20°C in 2-propanol
Specific gravity:	1.236 g/cm^3 at 20°C
Hydrolysis:	half-lives of 763 days, 28 days, and 2.2 days at pH 5, 7, and 9 respectively (Saakvitne, 1981).
Photolysis:	the half-life in irradiated aqueous solution was 88 days and the half-life of dark controls was 238 days. The half-life of samples irradiated during the growing season was calculated to be 66 days. The major degradation product was the sulfoxide (Kesterson, 1988)
Dissociation constant:	methiocarb has neither basic nor acidic properties in aqueous systems (Placke, 1988)
Thermal stability:	Stable at room temperature.
Volatility:	Henry's Law constant, H = 1.216 x 10^{-4} Pa.m^3.mol^{-1} at 20°C (Krohn, 1993)

Technical material

Purity:	>97.0%
Melting range:	not specified
Stability:	stable for 24 months at ambient temperature.

Formulations

The following formulations were identified from the information supplied by the manufacturer and by national governments: GR (40 g/kg); GR (20 g/kg); WP (500 g/kg); RB (40 g/kg)); GB (40 g/kg); RB (20 g/kg); SC (500 g/l).

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Studies were submitted on the metabolism of radiolabelled methiocarb in the rat, cow (2 studies), and chicken (2 studies).

Rat. The metabolism of [1-*phenyl*-^{14}C]methiocarb was investigated in rats (Stanley and Johnson, 1976). The same study was considered by the 1998 WHO Core Assessment Group of the JMPR. [1-*phenyl*-^{14}C]methiocarb dissolved in ethanol was administered at dose levels of 20 mg/kg body weight to a group

of 3 female rats and 0.25 mg/kg bw to 3 male and 3 female rats. Most of the administered radioactivity was excreted with the urine, >90 % in the high dose group and >70 % in the low dose group.

Only small amounts of unconjugated metabolites were found in rat urine. The major metabolites identified in the organosoluble fraction were methiocarb phenol (M03) and methiocarb sulfoxide phenol (M04). After enzymatic hydrolysis about half of the radioactive material in the urine was rendered organosoluble. Identification of metabolites was by thin-layer chromatography only. The enzymatic hydrolysis released about 8% methiocarb phenol, 23% methiocarb sulfoxide phenol, and 1% methiocarb sulfone phenol from the high dose group and 20% methiocarb phenol, 43% methiocarb sulfoxide phenol, and 1% methiocarb sulfone phenol from the low dose group. The percentages refer to the administered dose.

Cow. Two studies were submitted on the metabolism of [1-*phenyl*-^{14}C]methiocarb in the dairy cow. In one study (Minor and Murphy, 1977a), a dairy cow (500 kg) was dosed orally once by gelatin capsule with the test substance (4.83 mCi/mmole) at a rate of 0.14 mg/kg bw. Urine samples were collected 4, 8, 24, 48, 72, 96, 120, and 144 hours after dosing. Faeces, milk, and blood samples were also collected at various intervals. The urine samples collected within 48 hours were extracted with chloroform, and the residual aqueous fractions were buffered with 0.07 M pH 5 phosphate and subjected to sequential sulfatase-glucuronidase and acid hydrolysis (2 N HCl under reflux for 2 h). The enzymatic and acid hydrolysates were extracted with chloroform. All chloroform extracts were radioassayed and analysed by TLC only.

Within 144 hours of dosing, 96% of the administered radioactivity was eliminated in the urine. Faecal matter contained 1% and milk <1% of the initial radioactivity.

About 1% of the radioactivity in the urine was organosoluble. Enzyme treatment released 50-70% of the initial radioactivity, and acid hydrolysis released 10-25%. The main metabolites identified were methiocarb phenol (25-29%), methiocarb sulfoxide phenol (26-32%), and methiocarb sulfone phenol (20-23%).

In a more detailed study (Minor and Murphy, 1977b), one dairy cow (about 500 kg) was given [1-*phenyl*-^{14}C]methiocarb, 0.14 mg/kg bw/day (72 mg/day), for 5 consecutive days. The cow had received a single dose one week before the study. The cow was slaughtered within three hours of the final dosing, and samples of brain, heart, kidney, muscle, omental fat, renal fat, and udder were frozen and pulverized. Milk was taken in the morning and evening of each day. All samples were radioassayed. The radioactive residues in milk peaked (0.062 mg/kg) on the third day. The total radioactive residues in various tissues and milk are shown in Table 1.

Table 1. Total radioactive residue (TRR) after oral administration of [^{14}C]methiocarb to a dairy cow (Minor and Murphy, 1977a).

Sample	TRR, µg/g as methiocarb
Kidney	0.108
Liver	0.073
Udder	0.014
Heart	0.011
Renal fat	0.011
Muscle	<0.01
Omental fat	<0.01
Milk (day 3, evening)	0.062

A liver sample (20 g, containing 0.073 mg/kg as methiocarb) was homogenized with methanol/water, and the extract was partitioned with chloroform. The residual aqueous fraction was

refluxed with 1N HCl for 2 hours, partitioned with chloroform, refluxed for 2 hours with 6 N HCl, and partitioned again with chloroform. A kidney fraction (30 g, 0.108 mg/kg) was treated similarly, but the 1N HCl reflux was omitted. The extracts and residues were radioassayed, and the extracts were analysed by TLC on silica gel plates with two-dimensional development.

A milk sample, not otherwise identified, was homogenized with acetone and the filtrate was partitioned with chloroform. The aqueous fraction was subjected to sequential enzymatic and acid hydrolysis. Extracts were radioassayed and analysed by TLC.

Unlabelled standards were used to identify the radioactive spots on the plates, but with no confirmatory analysis, e.g. HPLC. The distribution of the radioactivity is shown in Table 2.

Table 2. Identity and distribution of radioactive residues in extracts of milk, liver, and kidney (Minor and Murphy, 1977a).

Compound	% of TRR								
	Milk					Kidney		Liver	
	Organo soluble	Enzyme hydrol.	Acid hydrol.	Aqueous residue	Lost[1]	Organo soluble	Acid hydrol.	Organo soluble	Acid hydrol.
Methiocarb	0	0	<1			<1	0	12	2
Methiocarb sulfoxide (M01)	3	0	<1			0	0	4	3
Methiocarb sulfone (M02)	<1	0	0			<1	0	<1	1
Methiocarb phenol (M03)	0	0	<1			11	44	14	11
Methiocarb sulfoxide phenol (M04)	<1	25	2			7	0	7	2
Methiocarb sulfone phenol (M05)	<1	25	1			16	1	3	3
Unknown	15	0	<1	16	9	2	1	3	9
Total	103					84		74	

[1] Lost during initial precipitation of milk proteins with acetone.

Poultry. Two studies were conducted on the metabolism of [*phenyl*-^{14}C]methiocarb in poultry. In the first study (Stanley *et al.*, 1979a), eight White Leghorn laying hens were orally dosed once with 4.4 mg radiolabelled methiocarb/kg bw. All eggs collected during each time period (1, 2, 3, 4, 5, 6, 24, 48, 72, and 96 hours) were pooled, when available, and radioanalysed. All residues were $\leq$0.02 mg/kg.

Excreta were collected and pooled at the same times as the eggs. Radioactivity was determined in the lyophilized samples. About 85% of the dose was excreted within 96 hours, with 84% excreted within 24 hours. Lyophilized excreta samples were homogenized with methanol/water and filtered. The filtrates were concentrated to remove methanol and extracted with methylene chloride. The residual water fractions were heated at 100°C with 2 N HCl for 1 hour. The fractions were radioassayed and analysed by TLC.

In the first 24 hour period, a total of 33% of the dose in the excreta were unconjugated metabolites (organosoluble), 39% were conjugated (acid-released), 8% were water-soluble. The unconjugated metabolites were tentatively identified as methiocarb (<1%), methiocarb phenol (13%), methiocarb sulfoxide phenol (9%), methiocarb sulfone phenol (7%), and hydroxymethyl-methiocarb

sulfoxide (2%). The conjugated metabolites were tentatively identified as methiocarb phenol (21%), methiocarb sulfoxide phenol (1%), and methiocarb sulfone phenol (10%).

In a second study (Stanley *et al.*, 1979b), the eight hens that had been treated previously with a single dose of radiolabelled methiocarb were utilized after a 3-week withdrawal period. [1-*phenyl*-^{14}C]methiocarb, 6.74 mCi/mmole, was administered at 4.4 mg/kg bw each day for 5 consecutive days. Eggs, collected each day, all contained <0.1 mg/kg ^{14}C as methiocarb. The birds were killed after the fifth dose, and composite tissue samples were radioassayed. The results are shown in Table 3.

Table 3. Radioactive residues in tissues and eggs after the oral administration of phenyl-labelled methiocarb to chickens (Stanley *et al.*, 1979b).

Sample	Residue, mg/kg as methiocarb
Kidney	3.3
Liver	2.0
Heart	0.8
Skin	1.3
Fat	0.7
Gizzard	7.7
Muscle	0.45
Eggs	<0.1

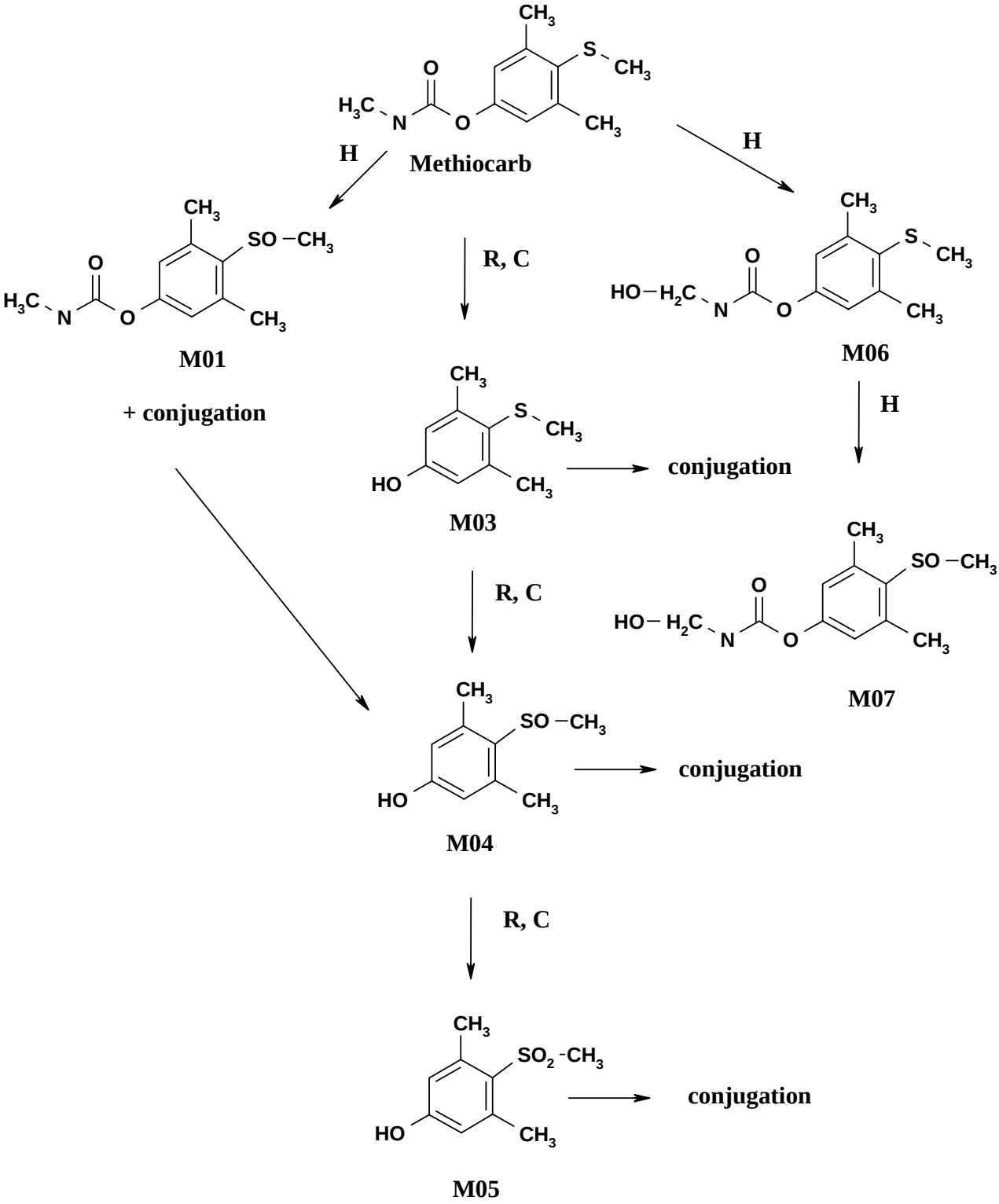
Tissue samples were extracted sequentially with organic solvents, and the residual water fractions were hydrolysed with 2 N HCl for 1 h at 100°C. This released 98% of the TRR from kidney, 92% from liver, 99% from fat and 98% from muscle. Extracts were analysed by two-dimensional TLC. There were no confirmatory analyses. Unlabelled standards were used to identify the radioactive spots. The findings are shown in Table 4.

Table 4. Identity and distribution of radioactive residues after oral administration of labelled methiocarb to chickens (Stanley *et al.*, 1979b).

Compound	% of TRR			
	Kidney	Liver	Fat	Muscle
Methiocarb	<1	<1	41	7
Methiocarb sulfoxide (M01)	<1	<1	1	5
Methiocarb phenol (M03)	2	7	14	8
M03 from acid hydrolysis	13	10	12	8
Methiocarb sulfoxide phenol (M04)	11	17	4	24
M04 from acid hydrolysis	18	7	5	4
Methiocarb sulfone phenol (M05)	4	9	2	2
M05 from acid hydrolysis	9	2	2	2
N-hydroxymethyl-methiocarb (M06)	<1	<1	7	5
N-hydroxymethyl-methiocarb sulfoxide (M07)	3	6	2	17
Total	60	58	90	82

The metabolic pathways proposed for methiocarb in animals are shown in Figure 1.

Figure 1. Proposed metabolic pathways of methiocarb in animals (C = chicken, H = hen, R-= ruminant).



Plant metabolism

Studies were provided on rice, tomato, lettuce, and apples. A rotational crop study was also submitted.

Àpples. A methiocarb WP formulation, 750 g/kg, containing [1-*phenyl*-^{14}C]methiocarb (10% of the total methiocarb) dissolved in water (101 g ai/100 l) was applied to run-off with a syringe to 24 apples on a dwarf Red Delicious apple tree in Kansas, USA (Morgan and Parton, 1974). The application was repeated 8 times at about 2-week intervals. The apples were harvested 14 days after the final treatment, or 77 days after the first application. Apples were also collected between applications.

In a separate experiment, a 50/50 mixture of radiolabelled and unlabelled methiocarb was dissolved in ethanol/water (266 g/100 l) and applied once at a rate of 750 µl/apple (2 mg methiocarb per apple) to each of 37 apples on another Red Delicious tree. The material was applied so as to avoid run-off. Apple samples were taken after 0, 4, 29, 36, and 43 days.

All apples were washed with benzene and separated into peel and pulp. Some peel fractions were extracted with acetonitrile/water (9:1), and others were hydrolysed with 0.1 N HCl for 30 min at 120°C. Three peeled apples were slurried with water and centrifuged, and the residual solid was extracted with acetone. The acetone and water extracts were combined and extracted with chloroform. A fraction of the water extract was also incubated with β-glucosidase and then hydrolysed with 0.1 N HCl as before.

Organic fractions were analysed by TLC only, using one solvent system (isopropyl ether/methanol, 8/1) and silica gel plates.

In the single application study, most of the radioactivity was in the benzene wash and decreased from 93% of the applied and 98% of the recovered activity on day 0 to 19% of the applied and 62% of the recovered radioactivity on day 43. The peel contained a maximum of 8.2% of the applied and 27% of the recovered radioactivity (on day 29). The organosoluble proportion of the peel residue decreased from 98% on day 0 to 36% on day 43, while the water-soluble proportion increased from 18% on day 4 to 54% on day 43. The insoluble residue was <10% at all times.

The residue in the pulp increased steadily from 0.04% of the applied ^{14}C to 4.8% of the applied and 16% of the recovered activity on day 29. The residue in the pulp slowly decreased or levelled off after day 29.

Without detailed substantiation, the “total residue” was characterized as methiocarb (65%), methiocarb sulfoxide (9%), and methiocarb sulfoxide phenol (18%).

In the multi-application study, the total radioactive residue in the apples was 8.04 mg/kg as methiocarb after 7 days and 4.52 mg/kg after 14 days. In the 14-day samples, 0.67 mg/kg (15% of the total radioactive residue) was in the pulp, and 82% of this was water-soluble.

Without detailed substantiation, it was stated that 95-97% of the benzene wash residue, 24% of the total radioactive residue, was methiocarb and 3-5% methiocarb sulfoxide. Methiocarb constituted 16% of the radioactive residue on the peel in the sample collected 14 days after the final application and methiocarb sulfoxide 1.4%. The peel contained 60% of the total radioactive residue. The residue on apples with the 14-day PHI was 4.52 mg/kg as methiocarb, consisting of 61% methiocarb, 6.5% methiocarb sulfoxide, 4.6% methiocarb phenol, 22% methiocarb sulfoxide phenol, and 1.1% methiocarb sulfone phenol.

Lettuce and tomatoes. A study on the uptake of radiolabelled methiocarb by lettuce and tomato plants was submitted (Strankowski and Murphy, 1976). Lettuce and tomato seedlings were treated with [1-*phenyl*-^{14}C]methiocarb, prepared as a 750 g/kg WP in water and applied at a rate of 1.12 kg ai/ha. The material

was applied to the ground (sand) and not to the aerial parts of the seedlings. Plants were harvested after 1, 3, 7, and 14 days, radioassayed and extracted. The extracts were analysed by TLC on silica gel plates.

The radioactivity was translocated rapidly in both lettuce and tomatoes, as indicated in Table 5. The major metabolites identified in the lettuce and tomato organic extracts were methiocarb (15–19 % on day 1, 1% on day 14), and methiocarb sulfoxide (34-52% on day 1, 2-3% on day 14). The enzymatic hydrolysis of aqueous fractions of lettuce seedlings at day 7 yielded methiocarb phenol and methiocarb sulfoxide phenol as 27% and 19% of the applied radioactivity respectively.

Table 5. Uptake of radiolabelled methiocarb by lettuce and tomato seedlings (Strankowski and Murphy, 1976).

Days after treatment	% of applied radioactivity[1]	
	Lettuce	Tomato
1	9	3
3	24	7
7	45	26
14	44	52

[1] Based on 50 µCi applied to each flat of seedlings.

Tomato. In separate experiments, tomato plants were grown in a greenhouse in nutrient solution and in soil. As the first fruits began to ripen, the radiolabelled methiocarb was applied at a rate of 1.12 kg ai/ha to the soil or nutrient solution. Tomatoes were harvested 1 and 7 days after addition of the methiocarb to the nutrient solution and 7, 14, 28, and 56 days after addition to the soil. Some leaves were also collected. The samples were radioassayed. The radioactivity in the tomato fruits grown in nutrient solution ranged from <0.007 to 0.013 mg/kg as methiocarb on day 1 and from 0.013 to 0.036 mg/kg on day 7. In the plants grown in soil the maximum residues in mature tomatoes were <0.007 mg/kg on day 7, 0.022 mg/kg on day 14, 0.066 mg/kg on day 28, and 0.025 mg/kg on day 56.

Rice. The metabolism of [1-*phenyl*-^{14}C]methiocarb in rice was reported (Strankowski, 1979). Rice was treated at planting with [1-*phenyl*-^{14}C]methiocarb formulated as a WP (750 g/kg) at a rate of 1.12 kg ai/ha. The aqueous mixture was applied as close to the exposed seeds as possible by pipette. Immature plants were harvested 14, 21, 28, and 35 days after treatment by cutting off the aerial portion at the ground.

In a separate plot, rice at the soft dough stage of grain maturity (132 days post-planting) was treated with radiolabelled methiocarb at a rate of 2.24 kg ai/ha. The mixture was formulated as a WP, 750 g/kg, and applied as a foliar spray. Plants were harvested 0, 1, 3, 6, 14, and 28 days after treatment. Nine days after the first application, some plants received a second treatment identical to the first and were harvested 0, 6, 14, 21, and 28 days after the second treatment. At each harvest the plants were separated into grain heads and stalks.

The same extraction procedure was used for all rice samples. The pulverized tissue was ultrasonicated with methanol/water and filtered. The filtrate was partitioned with chloroform, the aqueous fraction was incubated at 37°C for 20 hours with ß–glucosidase and then partitioned with chloroform. The aqueous layer was refluxed with 2 N HCl for 2 hours and again partitioned with chloroform. The solid residue from the initial extraction was also refluxed with 2 N HCl.

The extracts were analysed by one- and two-dimensional TLC on silica gel plates. Unlabelled standards were used for identifications, without confirmatory analyses. The distribution of the recovered radioactivity in the rice treated at planting is shown in Table 6, and that in the grain and stalks after foliar application is shown in Table 7.

Table 6. Distribution of ^{14}C in young rice plants after application of [^{14}C]methiocarb to seeds and soil at planting (Strankowski, 1979).

Days after treatment	% of recovered radioactivity[1]						
	Organo-soluble	Aqueous			Insoluble		
		Enzyme hydrol.	Acid hydrol.	Aqueous (not released)	Acid hydrol.	Aqueous (not released)	Not extracted
14	72	8	11	1	NA	NA	8
21	66	12	9	1	NA	0	12
28	61	NA	NA	24	9	3	2
35	61	6	12	1	14	4	2

NA = not analysed
[1]Extracts and extracted fractions were radioassayed, not initial samples. Thus, the reported values are percentages of the recovered radioactivity, not necessarily of the total radioactive residue in the plants.

Table 7. Distribution of ^{14}C in rice after foliar application (Strankowski, 1979).

Days after lst spraying	% of recovered radioactivity[1]						
	Organo-soluble	Aqueous			Insoluble		
		Enzyme hydrol.	Acid hydrol.	Aqueous (not released)	Acid hydrol.	Aqueous (not released)	Not extracted
Rice grain							
0	99	NA	NA	<1	NA	NA	1
14	75	NA	NA	10	12	2	1
28	63	NA	NA	9	20	5	3
Stalks							
0	98	NA	NA	1	NA	NA	1
14	85	NA	NA	7	NA	NA	8
28	72	2	7	2	13	3	2
Days after 2nd spraying							
Stalks							
0	95	NA	NA	2	NA	NA	3
14	83	NA	NA	7	NA	NA	10
28	68	NA	NA	9	17	3	3
Grain							
0	96	NA	NA	2	NA	NA	2
14	80	2	5	6	NA	NA	11
28	67	NA	NA	7	18	3	4

NA = not analysed
[1]Extracts and extracted fractions were radioassayed, not initial samples. Thus, the reported values are percentages of the recovered radioactivity, not necessarily of the total radioactive residue in the plants.

The compounds were identified by TLC only in both experiments. In the young rice plants harvested 14, 21, 28, and 35 days after soil/seed treatment methiocarb was a minor component, about 2% of the recovered radioactivity. The major metabolite at all intervals was methiocarb sulfoxide, 36-47%. Other significant metabolites were methiocarb phenol conjugate, 4-15%, methiocarb sulfoxide phenol 3-6%, methiocarb sulfoxide phenol conjugate 8-11%, and methiocarb sulfone phenol conjugate 3-5%.

The compounds identified in the rice and stalks after one or two foliar treatments are shown in Table 8.

Table 8. Identified compounds in rice after foliar application of radiolabelled methiocarb (Strankowski, 1979).

Compound	^{14}C, % of total recovered in extracts and fractions					
	Days after 1st spraying					
	0	1	3	6	14	28
GRAIN						
Methiocarb (M)	94	92	88	78	41	11
Methiocarb sulfoxide (M01)	2	4	5	12	25	32
Methiocarb sulfone (M02)	-	-	<1	1	1	3
Methiocarb sulfoxide phenol (M04)	<1	<1	<1	1	4	11
Methiocarb sulfone phenol (M05)	1	1	1	1	1	1
N-hydroxymethyl methiocarb sulfoxide (M07)	-	-	-	-	2	3
M03 conjugate	-	-	-	-	4	1
M04 conjugate	-	-	-	-	-	<1
M05 conjugate	-	-	-	-	1	2
	Days after 2nd spraying					
	0	1	6	14	28	NA
Methiocarb (M)	86	64	41	26	18	
Methiocarb sulfoxide (M01)	7	17	26	31	31	
Methiocarb sulfone (M02)	-	1	1	1	1	
Methiocarb sulfoxide phenol (M04)	1	2	5	9	9	
Methiocarb sulfone phenol (M05)	1	1	1	1	1	
N-hydroxymethyl methiocarb sulfoxide (M07)	<1	1	3	3	2	
M03 conjugate	-	-	2	9	10	
M04 conjugate	-	-	1	1	1	
M05 conjugate	-	-	1	2	2	
STALKS						
	Days after 1st spraying					
	0	1	3	6	14	28
Methiocarb (M)	90	88	81	70	42	20
Methiocarb sulfoxide (M01)	6	7	10	17	32	36
Methiocarb sulfone (M02)	-	-	-	<1	1	1
Methiocarb sulfoxide phenol (M04)	<1	1	2	3	4	10
Methiocarb sulfone phenol (M05)	1	1	1	1	1	2
N-hydroxymethyl methiocarb sulfoxide (M07)	-	-	<1	1	1	-
M03 conjugate	-	-	-	-	-	9
M04 conjugate	-	-	-	-	-	2
M05 conjugate	1	1	1	1	1	2
	Days after 2nd spraying					
	0	6	14	21	28	NA
Methiocarb (M)	80	54	34	27	15	
Methiocarb sulfoxide (M01)	10	22	35	35	35	
Methiocarb sulfone (M02)	0	1	1	1	1	
Methiocarb sulfoxide phenol (M04)	2	4	8	12	10	
Methiocarb sulfone phenol (M05)	2	1	1	2	1	
N-hydroxymethyl methiocarb sulfoxide (M07)	<1	1	-	-	2	
M03 conjugate	-	-	-	6	9	
M04 conjugate	-	-	-	2	1	
M05 conjugate	2	1	1	2	1	

NA = not analysed

A rotational crop study was conducted with [1-*phenyl*-^{14}C]methiocarb (Strankowski and Kottman, 1979). Radiolabelled methiocarb, formulated as WP 750 g/kg was incorporated into sandy loam soil (74% sand, 16% silt, 10% clay) at a rate of 5.6 kg ai/ha, and sweet corn was planted immediately as the primary crop. The sweet corn was harvested at normal maturity, and the land lay fallow until the next crop year. Rotational crops of wheat, sugar beet, and spinach were then planted. The crops were sampled at specific times through normal harvest, and the samples were radioassayed.

Mature samples of wheat heads, wheat stalks, wheat forage, sugar beet roots, and spinach were extracted with methanol/water and partitioned with chloroform. The extracts were analysed by one-dimensional TLC on silica gel plates. Unlabelled standards were used to identify the compounds. The results are shown in Table 9.

Table 9. Radioactive residues in one-year rotational crops grown in soil treated with [^{14}C]methiocarb at 5.6 kg ai/ha (Strankowski and Kottman, 1979).

Days after application	Methiocarb equivalents, mg/kg					
	Wheat			Sugar beet		Spinach
	Heads	Stalks	Forage	Tops	Roots	
399			0.150	0.108		
426			0.195	0.053	0.309	0.184
436			0.251	0.052	0.380	0.138
450				0.071	0.252	0.225
468				0.052	0.099	0.150
478						0.084
551	0.066	0.141	0.323			

The metabolites identified in the organosoluble extracts of wheat and spinach are shown in Table 10. No results for sugar beet were reported. Details of the identification procedures were not provided.

Table 10. Metabolites in rotational crops after treatment of soil with radiolabelled methiocarb (Strankowski and Kottman, 1979).

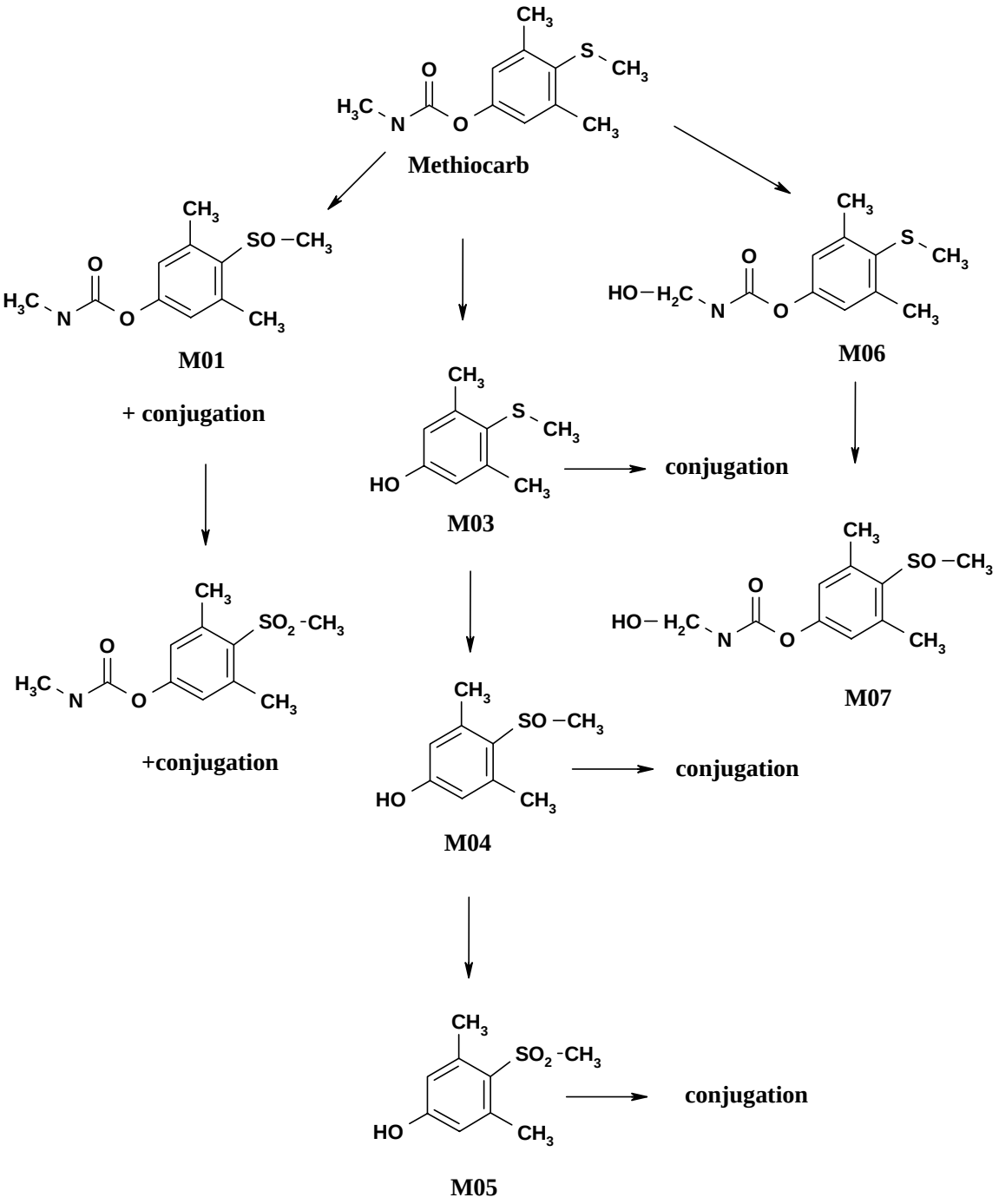
Compound	Sample							
	Wheat head (551 days)		Wheat stalk (551 days)		Wheat forage (551 days)		Spinach (450 days)	
	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg
N-hydroxymethyl-methiocarb	12	0.008	3	0.004	1	0.003	7	0.016
Methiocarb sulfoxide	6	0.004	4	0.006	12	0.039	0	0
Methiocarb sulfoxide phenol	14	0.009	7	0.010	6	0.019	26	0.058
N-hydroxymethyl-methiocarb sulfoxide	5	0.003	3	0.004	2	0.006	0	0
Methiocarb sulfone	11	0.007	8	0.011	10	0.032	0	0
Methiocarb sulfone phenol	0	0	0	0	0	0	2	0.005

A second rotational crop study was conducted with unlabelled methiocarb (Murphy and Morris, 1979). Methiocarb WP was applied to bare soil at rates of 1.4, 2.8, 5.6, and 11.2 kg ai/ha in Florida (sand) and Kansas (silty clay loam). Rotational crops were planted 30, 60, 90, 120, and 365 days after soil treatment. In Kansas sorghum, wheat, snap beans, peas, carrots and radishes were planted, and in Florida maize, black-eyed-peas and turnips. The crops were harvested at normal maturity and green forage samples of the cereals and green vines were taken during the growing season.

Samples were analysed for the combined residue of methiocarb, methiocarb sulfone and methiocarb sulfoxide. No residues (<0.02 mg/kg) were found in any edible portion of the vegetables or grain planted 30 or more days after any application of methiocarb to the soil, but some were found in green vines and green forage after application at 11.2 kg ai/ha. Maize forage from planting 30 days after treatment had a residue of 0.14 mg/kg; black-eyed pea vines had 0.15 mg/kg from the 30-day planting and 0.07 mg/kg from 90 days. Turnip tops from planting at 60 days had residues of 0.29 mg/kg.

The suggested metabolic pathways of methiocarb in plants are given in Figure 2.

Figure 2. Proposed metabolic pathways of methiocarb in plants.



Environmental fate in soil

Studies were provided on aerobic and anaerobic degradation, photolysis, adsorption of methiocarb, methiocarb phenol and methiocarb sulfoxide, and leaching of methiocarb.

The fate of methiocarb in sandy loam soil was studied by Stanley and Flint (1983). Soil was air-dried and milled. A 5.0 kg sub-sample, pH 7.3, was mixed with a benzene solution of [1-*phenyl*-^{14}C]methiocarb, [*methylthio*-^{3}H]methiocarb and unlabelled methiocarb at 7.5 mg/kg, equivalent to 11.5 kg ai/ha. The treated soil was placed in a plastic pan in a greenhouse and water was added weekly.

Five g soil samples were taken at 1, 2, 4, 8,12 and 16 weeks after treatment. The samples were extracted with methanol/water and the extracts partitioned with chloroform. The proportion of extractable radioactivity decreased from 76% at week 4 to 67% at week 16. The residual soils were heated under nitrogen in a steam bath with 1 N HCl for 2 hours, and the mixtures were centrifuged and decanted. The solids were washed with water and the combined acid extracts and water washes partitioned with chloroform. The acid treatment released 14-19% of the applied radioactivity.

The extracts were analysed by TLC, using three different solvent systems. $^{3}H:C^{14}$ ratios of individual components were use to confirm chromatographic identifications. The results are shown in Table 11.

Table 11. Distribution of radioactive residues in soil treated with methiocarb at a rate of 7.5 mg/kg (Stanley and Flint, 1983).

Compound	Radioactivity, % of applied, mg/kg as methiocarb			
	4 wks	8 wks	12 wks	16 wks
Methiocarb (organosoluble)	49/3.7	38/2.9	27/2.9	30/2.3
Methiocarb (acid released)	1.0/3.7	1.1/0.08	0.8/0.06	0.9/0.07
Methiocarb sulfoxide (organosoluble)	10/0.8	13/1.0	12/0.9	13/1.0
Methiocarb sulfoxide (acid released)	9.7/0.74	11/0.81	9.5/0.71	9.5/0.71
Methiocarb sulfoxide phenol (organosoluble)	5.3/0.4	10/0.8	11/0.9	15/1.1
Methiocarb sulfoxide phenol (acid released)	0.5/0.04	0.7/0.05	1.0/0.08	0.8/0.06
Methiocarb sulfone + methiocarb phenol + methiocarb sulfone phenol (organosoluble)	0.4/0.04	1.8/0.13	1.8/0.13	1.9/0.14
Methiocarb sulfone + methiocarb phenol + methiocarb sulfone phenol (acid released)	0.5/0.04	0.5/0.04	1.2/0.09	0.3/0.02

The degradation of [1-*phenyl*-^{14}C]methiocarb was further investigated under both aerobic and anaerobic conditions (Minor and Freeseman, 1989). The methiocarb was added as an ethanol solution to dry sandy loam soil at a concentration of 1.4 mg/kg dry soil. Replicate 100 g samples, pH 6.7, were prepared and stored in the dark at 24 $\pm$ 2˚C. Duplicate soil samples were extracted in a Soxhlet apparatus with chloroform/methanol after 0, 1, 3, 7, 14, 29, 64, 91 and 217 days, and analysed by HPLC. A 91-day sample was extracted with methanol and then refluxed for 2 hours with 2N HCl. The hydrolysate was partitioned with acetone/chloroform.

Extractable ^{14}C decreased from 100% of the applied radioactivity on day 0 to 27% on day 217 and bound residues increased from 0% on day 0 to 43% on day 217. Significant $^{14}CO_2$ appeared after 29 days and increased from 5% to 30% of the applied radioactivity by day 217. The recovery of ^{14}C approached 100% at all intervals.

The degradation was rapid, with methiocarb decreasing from 96% of the total radioactivity on day 0 to 3% on day 217, and biphasic. The first phase showed a half-life of 17.7 days and the second 111 days, assuming that the degradation followed first-order kinetics.

The compounds identified in the soil under aerobic conditions are shown in Table 12. The identity of methiocarb sulfone quinone was confirmed by GC-MS.

Table 12. Extractable radioactive compounds in sandy loam treated with [^{14}C]methiocarb (1.45 mg/kg) and incubated in the dark under aerobic conditions (Minor and Freeseman, 1989).

Time (days)	^{14}C, % of total applied							
	Extract-able	Methio-carb	Methio-carb phenol	Methio-carb sulfoxide	Methiocarb sulfoxide phenol	Methiocarb sulfone	Methiocarb sulfone phenol	Methiocarb sulfone quinone
0	100	96	2	2	0	0	0	0
1	98	91	0	7	<1	0	0	0
3	96	83	0	13	<1	0	0	0
7	94	70	0	21	3	0	0	0
14	84	48	0	28	8	0	0	0
29	75	24	0	30	16	1	3	0
64	50	8	0	13	18	1	7	2
91	44	6	0	8	15	1	9	3
217	27	3	0	2	7	0	7	8

To study anaerobic conditions, two 14-day aerobic samples were covered with water (pH 5) and purged continuously with nitrogen. At 0, 15, 29 and 64 days after the addition of water, samples were extracted in a Soxhlet apparatus with chloroform/methanol and the extracts analysed by HPLC and TLC. An aliquot of extracted 29-day soil was refluxed with methanol, and a separate aliquot was refluxed sequentially with 1 N HCl, 2 N HCl and 5N HCl.

Under anaerobic conditions there was little change in the proportion of extractable radioactivity, which decreased from 87% to 76% between day 0 and day 64. Volatiles never exceeded 4% of the applied radioactivity. The half-life of methiocarb was calculated to be 64 days (first-order kinetics). The identified compounds are shown in Table 13.

Table 13. Extractable radioactive compounds in sandy loam soil treated with [^{14}C]methiocarb and incubated in the dark under anaerobic conditions (Minor and Freeseman, 1989).

Time, days	^{14}C, % of total applied						
	Extract-able	Methio-carb	Methiocarb phenol	Methiocarb sulfoxide	Methiocarb sulfoxide phenol	Methiocarb sulfone	Methiocarb sulfone phenol
0	87	55	0	24	8	0	0
15	82	43	31	3	5	0	<1
29	80	37	37	2	3	0	<1
64	76	27	47	1	1	<1	<1

A similar anaerobic experiment was conducted with [1-*phenyl*-^{14}C]methiocarb sulfoxide, which was hydrolysed to methiocarb sulfoxide phenol within 3 days. After 49 days, methiocarb phenol was the major product.

On the basis of a study which was not available for submission the manufacturer provided detailed calculations of the half-lives of methiocarb and its degradation products under aerobic conditions in different soils (Schad, 1998). The results are shown in Table 14.

Table 14. Half-lives of methiocarb and its degradation products in various soils at 20°C under aerobic conditions (Schad, 1998).

Soil	Half-life, days				
	Methiocarb	Methiocarb sulfoxide	Methiocarb sulfoxide phenol	Methiocarb sulfone phenol	Compound 6 (structure unknown)
BBA2.2 (loamy sand)	1.6	6.3	2.2	20	54
Frankenforst	1.4	1.6	9.4	3.0	14
Höfchen (silt)	1.0	3.0	4.2	2.5	33

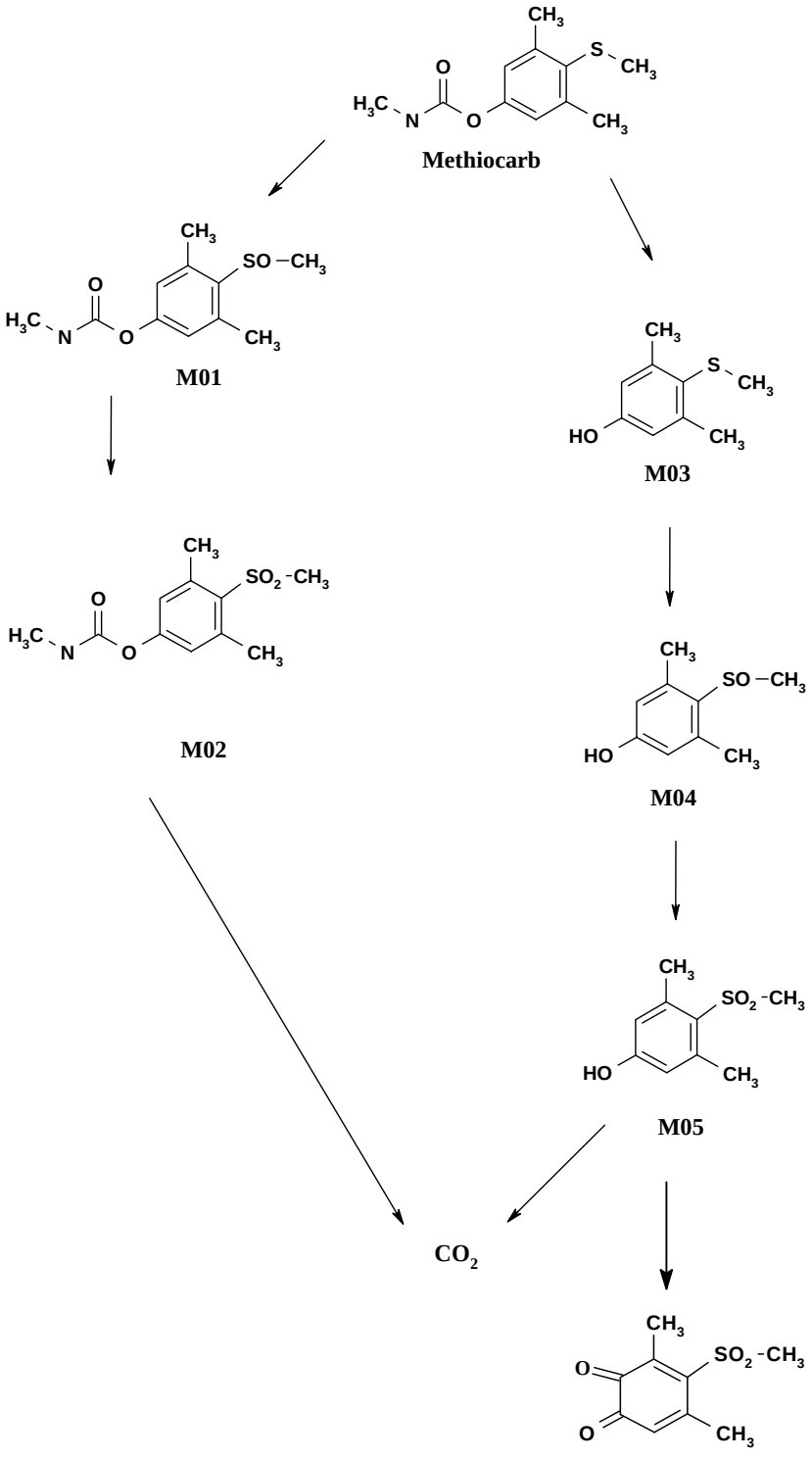
The photolysis of added methiocarb on a soil surface under natural sunlight was studied by Jackson *et al.* (1988) who added [1-*phenyl*-^{14}C]methiocarb to sandy loam soil (3.1 g) in 60 mm Petri dishes at a rate of 9.1 µg/g, or 28 µg/dish. The dishes were exposed to natural sunlight in Lexington, Kentucky, USA for 30 days. Dark control samples were also prepared. The mean temperature of the irradiated plates was 21.6 $\pm$ 1.4°C. The light intensity varied considerably over the 30 days, between 39 and 38909 µW/cm^2.

The soils were sampled on days 0, 5, 10, 15, 20 and 30. The soil samples were extracted with chloroform/methanol and the extracts and residual soils were radioassayed. The total recovery of radioactivity ranged from 80.5 (88.9% average of duplicates) to 104.4%, mean 98.2% $\pm$ 4.87%. Measured volatiles were insignificant. The extracts were analysed by HPLC, with confirmation by TLC.

Methiocarb was the major component of the residue at all times in both control and irradiated samples, accounting for 47% of the radiolabelled residue on irradiated soil and 75% on control soil after 30 days. The major degradation product was methiocarb sulfoxide, 23% of the residue on irradiated soil and 3.1% on control soil at 30 days. Methiocarb sulfoxide phenol was a minor component, 3.7% on irradiated soil at day 30 and not detected on the control soil. The residue not extracted by organic solvents was 10-15% of the total radiolabelled residue in irradiated soil <10% in control soil.

The results indicated that degradation was due to photolytic and other processes. The half-lives were 28 days for irradiated samples and 81 days for control samples.

Figure 3. Proposed degradation pathways of methiocarb in soil.



Ridlen and Pfankuche (1987a) studied the adsorption of [1-*phenyl*-^{14}C]methiocarb by soil. Duplicate portions of four soils (1.0 to 2.5 g) in individual silanized-glass culture tubes were mixed with 10 to 20 ml of treatment solutions containing 0.4, 0.8. 2.0 and 4.0 mg/l methiocarb, each 0.02 µCi/ml. The tubes were sealed and shaken gently in a horizontal position at 27 ± 2°C. The supernatants were sampled after 2, 6, 24 and 48 hours. After 48 hours the supernatants were removed and replaced by 0.01 M calcium chloride solution, and the linear shaking was resumed for an additional 5 days. The supernatants were extracted with chloroform and the extracts analysed by TLC on silica gel. The residual solids were radioassayed.

The methiocarb reached adsorption equilibrium in the water/soil systems within about 24 hours. Analyses of the water fractions revealed no significant degradation of the methiocarb. Freundlich adsorption and desorption constants were calculated (Table 15). The high K_d and K_{oc} values indicate adsorption of methiocarb to all the soils and low leaching potential.

Table 15. Soil adsorption and desorption coefficients of methiocarb (Ridlen and Pfankuche, 1987a).

Soil	Adsorption		Desorption	
	K_d	K_{oc}	K_d	K_{oc}
Sand (pH 4.3)	5.3	1000	8.2	1547
Sandy loam (pH 4.9)	4.3	632	6.7	985
Silt loam (pH 5.9)	9.0	600	16.2	1080
Clay loam (pH 6.3)	4.9	408	8.1	675

K_{oc}: >5000 immobile; 2000-5000 very low mobility; 500-2000 low mobility; 150-500 moderate mobility; <150, high mobility.

The adsorption of [1-*phenyl*-^{14}C]methiocarb sulfoxide was also studied by Ridlen and Pfankuche (1987b). The soils, pH 4.3-6.3, were treated with the radiolabelled methiocarb sulfoxide at a rate of 1.6 mg/kg, an approximation to a field application rate of 4.5 kg ai/ha, by mixing soil (2 g) in silanized-glass culture tubes with the radiolabelled methiocarb sulfoxide in 0.01 M aqueous calcium chloride solution (8 ml). The tubes were shaken continuously at 27 ± 2°C and the supernatants were sampled after 0.5, 2, 4 and 24 hours and extracted with chloroform. The supernatants were removed from the 24-hour samples and the residual soils were shaken with calcium chloride solution saturated with unlabelled methiocarb sulfoxide (to remove residual test solution) and extracted with chloroform. The experiment was repeated with a treatment solution containing 0.01 M potassium hydrogen phosphate adjusted to pH 4 with hydrochloric acid.

Liquid samples were radioassayed and the extracts were analysed by TLC. Only methiocarb sulfoxide phenol was found in the soil extracts after 24 hours. The amount of methiocarb sulfoxide adsorbed to the soil was below the level of detection of the analytical method, 0.05 µg/g. With the assumption that this was the concentration of methiocarb sulfoxide in the soils, the adsorption coefficients were calculated. They ranged from 0.2 mg/kg for sand and sandy loam to 0.5 mg/kg for silt loam, showing that methiocarb sulfoxide was poorly adsorbed to the soils. The aqueous phase of both the calcium chloride and the phosphate buffer systems contained methiocarb sulfoxide and methiocarb sulfoxide phenol, with the latter accounting for as much as 41% of the radioactivity (on silt loam) in the aqueous phase.

The adsorption of [1-*phenyl*-^{14}C]methiocarb sulfoxide phenol was investigated in calcium chloride solution at concentrations of 0.04, 0.21, 1.01 and 5.14 mg/l (Fent, 1996). Twelve g of each soil was mixed with 20 ml of test solution and shaken for 24 hours at 20 ± 1°C. The supernatants were removed and the residual soils shaken with 20 ml of 0.01 M calcium chloride solution. HPLC analyses of the supernatants after the 24-hour period indicated that >99% of the radioactivity could be assigned to unchanged methiocarb sulfoxide phenol. Freundlich adsorption and desorption constants are shown in Table 16.

Table 16. Adsorption and desorption coefficients for methiocarb sulfoxide phenol on four soils (Fent, 1996).

Soil	Adsorption		Desorption	
	K_d	K_{oc}	K_d	K_{oc}
Sand (pH 5.3)	0.1885	26.9	0.7384	105.5
Sandy loam (pH 6.3)	0.6611	26.7	1.5240	61.5
Silt loam (pH 7.3)	0.4342	48.2	1.3828	153.6
Silty clay (pH 7.4)	0.6466	101.0	1.6438	256.8

K_{oc}: 50-150, high mobility; 150-500, medium mobility, >500, low mobility

The leaching of [1-*phenyl*-^{14}C]methiocarb, specific activity 33.7 mCi/mmole, added as a water/acetonitrile solution to sandy loam soil that had been air-dried was reported (Ridlen, 1987). The concentration of methiocarb in the soil was 37 mg/kg. The moisture content of the soil was adjusted to 75% by the addition of water, and the soil mixture was aged for 30 days at 22-25°C under aerobic conditions. The moisture content was adjusted to 75% each week. No volatiles (<1% of total radioactivity) were detected during the ageing process. The aged soil (50 g) was extracted sequentially with chloroform and chloroform/methanol (Soxhlet). The combined extracts were concentrated and analysed by TLC. The residue in the aged soil consisted of 80% methiocarb, 7% methiocarb sulfoxide and 6% methiocarb sulfoxide phenol. About 6% of the total radioactivity remained in the soil after extraction.

Glass columns were packed with sea sand (100 g), air-dried test soil (30 cm) and the aged soil (20 g). The columns were saturated with 0.01 M aqueous calcium chloride and 1.1 l of 0.01 M aqueous calcium chloride solution was dripped continuously through the column over a 5-day period. The leachates were collected in 220 ml fractions and radioassayed, aliquots were extracted with chloroform, and the concentrated extracts were analysed by TLC. The used soil columns were frozen, segmented and radioassayed.

The distribution of the radioactivity in the soil columns and the leachates is shown in Table 17.

Table 17. Distribution of radioactivity in soil columns and leachates from soil treated with radiolabelled methiocarb and aged aerobically for 30 days (Ridlen, 1987).

Fraction	% of applied radioactivity[1]		
	Sand (pH 4.3)	Sandy loam (pH 5.0)	Silty loam (pH 5.9)
Applied aged soil	10	14	13
Column section			
0-5 cm	7	23	33
5-10 cm	11	21	17
10-15 cm	16	19	15
15-20 cm	13	7	9
20-25 cm	10	4	5
35-30 cm	4	4	1
Total soil	71	92	93
Leachate	23	7	3
Sand	<1	<1	<1
Used column wash	0	0	0
Total radioactivity accounted	94	99	96

[1] Average of 3 determinations on each of two soil columns.

In the leachate from the sand soil column 2% of the applied ^{14}C represented methiocarb, 12% methiocarb sulfoxide, 7% methiocarb sulfone and 1% methiocarb phenol. In the sandy loam leachate 2% represented methiocarb sulfoxide, 3% methiocarb sulfoxide phenol and 1% methiocarb phenol. In the silty loam leachate 1% of the applied ^{14}C was associated with methiocarb sulfoxide phenol.

Environmental fate in water

The fate of [1-*phenyl*-^{14}C]methiocarb in aerobic and anaerobic aquatic systems was investigated by Minor and Atwell (1979). The radiolabelled methiocarb was applied to pond water (100 ml) in glass jars at 2 mg/l for the aerobic study. For the anaerobic study, soil (100 g; 16% sand, 54% silt, 30% clay) was also added to each jar. The jars were wrapped in black plastic and maintained in a greenhouse environment. The temperature range was not reported. Jars were removed at intervals and the contents analysed. The aerobic and anaerobic pond water was radioassayed and extracted with ethyl acetate, and the extract was concentrated and analysed by TLC. The anaerobic samples were separated into soil and water fractions and the soils Soxhlet-extracted with chloroform/methanol. The soil residues were further extracted with 0.5 N NaOH. Extracts were analysed by one- and two-dimensional TLC.

At least 95% of the applied radioactivity in the aerobic samples and 84% in the anaerobic samples (29% of the radioactivity in the water fraction and 55% in the soil fraction) was organosoluble at day 21. By day 56, 42% of the radioactivity was bound to the soil and 22% was not recovered. The results are shown in Table 18. In the aerobic system the parent compound disappeared within 3 days. In the anaerobic environment 5% remained at day 3. The major products were methiocarb sulfoxide phenol and methiocarb phenol (63% and 34% respectively at day 14) in the aerobic system, and methiocarb phenol (51% in the soil, 21% in the water at day 28) in the anaerobic system.

Table 18. Radioactive residues in methiocarb-treated aquatic systems (Minor and Atwell, 1979).

Time, days	^{14}C, % of applied									
	Aerobic				Anaerobic					
	Water				Water			Soil		
	Methiocarb	Methiocarb phenol	Methiocarb sulfoxide phenol	Methiocarb sulfoxide	Methiocarb	Methiocarb phenol	Methiocarb sulfoxide	Methiocarb	Methiocarb phenol	Methiocarb sulfoxide phenol
0	97	1	0	1	97	1	1	-	-	-
3	0	80	20	0	18	45	0	10	14	<1
7	0	83	17	0	5	42	0	9	32	<1
14	0	34	63	0	2	35	0	6	34	
21	-	-	-	-	<1	28	0	5	48	1
28	-	-	-	-	<1	21	0	4	51	2
32	-	-	-	-	-	-	-	-	-	-
56	-	-	-	-	<1	2	0	3	26	1
112	-	-	-	-	0	0	0	1	3	<1

The fate of [1-*phenyl*-^{14}C]methiocarb was studied in buffered aqueous solutions maintained in the dark at 25°C (Saakvitne *et al.*, 1981). The solutions were quantified by radioanalysis and TLC. Half-lives were calculated for methiocarb assuming first-order kinetics (Table 19).

Table 19. Half-life values for the hydrolysis of [1-*phenyl*-^{14}C]methiocarb in sterile aqueous buffer solutions (Saakvitne *et al.*, 1981).

pH	Half-life, days, at 25˚C
5	763
7	28
9	2.2

At pH 5 the main product was methiocarb sulfoxide (<1-9%, days 0-51), and methiocarb accounted for 91-97% of the applied radioactivity. At pH 7 the major product was methiocarb phenol (46% at day 30) and at pH 9 methiocarb phenol (78% at day 7) and methiocarb sulfoxide phenol (10% at day 7). Minor products were about 1% *N*-hydroxymethyl-methiocarb sulfone (M08) and 2% *N*-hydroxymethyl-methiocarb (M06) at pH 9, and about 1% *N*-hydroxymethyl-methiocarb at pH 5 and pH 9.

The photochemical degradation of [1-*phenyl*-^{14}C]methiocarb was investigated in pH 5.0 aqueous solutions exposed to natural sunlight for 30 days in Kentucky, USA (Kesterson *et al.*, 1988). Replicate quartz tubes, both irradiated and dark controls, were maintained at 25°C and removed for analysis by radioassay and HPLC at 0, 0.25, 6, 12, 20 and 30 days. The HPLC identifications were confirmed by TLC. The mean total recovery of the radiocarbon from all samples was 102 $\pm$ 11.4%. Excluding one dark control, the recoveries ranged from 80% to 110%.

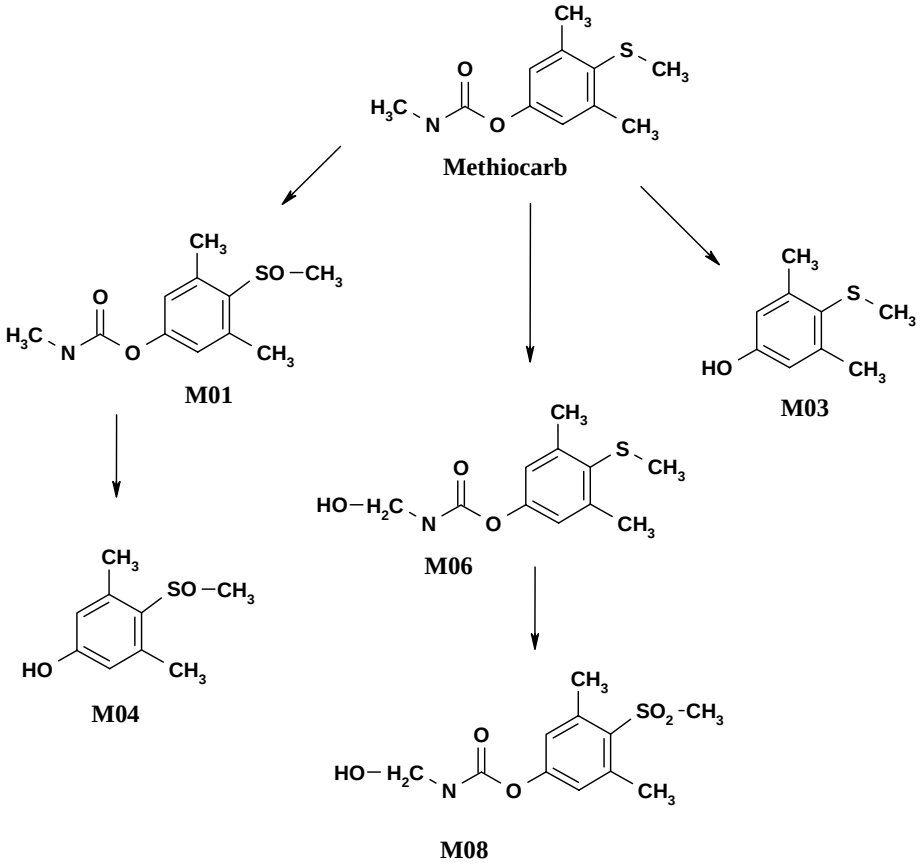
The only product found in both the irradiated and dark control tubes through day 20 was methiocarb sulfoxide, at a maximum of 1% in the control and 13% in the irradiated solutions. On day 30 a new product appeared, methiocarb sulfoxide phenol at a maximum of 3% in the irradiated and 0.8% in the control solutions.

The photolysis half-life was calculated to be 88 days, or 128 days when corrected for non-photolytic degradation.

The quantum yield for the direct photodegradation of methiocarb in water was calculated from the UV absorption data and the kinetic results of two photodegradation experiments in a merry-go-round irradiation apparatus to be 0.2825 (Hellpointner, 1989). This quantum yield was combined with UV absorption data to estimate the environmental half-life of methiocarb as a result of direct phtotodegradation in water. In spring and summer, the half-life was estimated to range from 4 to 19 days, depending on the latitude.

Proposed degradation pathways are shown in Figure 4.

Figure 4. Proposed degradation pathways of methiocarb in the aquatic environment.



METHODS OF RESIDUE ANALYSIS

Analytical methods

The government of The Netherlands supplied an official multi-residue method 1 (MMR1: Analytical Methods for Pesticide Residues in Foodstuffs, Ministry of Health, Welfare and Sport, 1996). Non-fatty samples such as fruits and vegetables are macerated with acetone and methylene chloride. There is no oxidation of methiocarb and its metabolites to a common compound. The concentrated extract is analysed by gas chromatography on a 30 m x 0.25 mm capillary column with a flame photometric or ion trap detector. The general recovery range is 80-100% and the limit of determination is <0.1 mg/kg.

In Bayer Method 171 (Thornton and Dräger, 1973) crop samples (100 g) are extracted with acetone and 0.05 N HCl. The filtrate is extracted with chloroform and the extract concentrated to dryness. The residue is dissolved in acetone (40 ml) and precipitated with an aqueous solution of ammonium chloride and phosphoric acid. The filtrate is extracted with chloroform (3 x 50 ml) and the extract concentrated to dryness, dissolved in acetone and oxidized with 0.1 M potassium permanganate (15 minutes at room temperature). The resulting sulfone is silylated. The derivative is injected into a gas chromatograph equipped with a 2 ft x 4 mm i.d. glass column packed with 5% DC 200 on Gas Chrom Q and operated isothermally at 170°C with a flame photometric detector in the sulfur mode. Calibration is by external oxidized and derivatized standards, 5 to 100 ng. A log-log calibration curve is used. A linear response can be obtained down to 0.03 mg/kg, in milk to 0.005 mg/kg. The absolute limit of detection is 0.01 mg/kg for all samples except milk.

Milk (200 ml) is blended with acetone (400 ml) and Hyflo Super-Cel (10 g). The filtrate is partitioned with chloroform. The chloroform extract is concentrated to dryness, and the residue dissolved in hexane and partitioned with acetonitrile. The acetonitrile extract is concentrated to dryness and oxidized as above. The residue from the oxidation step is dissolved in benzene and transferred to a Florisil column which is eluted sequentially with benzene and benzene/acetonitrile (95/5). The later eluate is concentrated to dryness and analysed as above.

Animal tissues (50 g) are chopped and blended with acetonitrile (200 ml). The mixture is filtered and the tissue is blended with hexane (200 ml). The combined extracts are shaken and the acetonitrile phase is washed with fresh hexane and analysed as above.

Recoveries from fortified samples are shown in Table 20. Each recovery is from one sample except where otherwise noted.

Table 20. Recoveries of methiocarb and metabolites from fortified commodities by Method 171 (Thornton and Dräger, 1973).

Sample	mg/kg added	Recovery, %		
		Methiocarb	Methiocarb sulfoxide	Methiocarb sulfone
Apple peel	0.5	88	90	120
	0.1	79	80	96
	0.05	118	86	68
Apple pulp	0.1	117	108	96
	0.05	78, 120	104, 98	82, 120
Maize kernels	0.1	120	70	70
	0.05	84, 88, 92	72, 91, 83	71, 73, 72
Maize forage	0.1	80	80	80
	0.05	100	-	-
Sugar beet tops	0.5	102, 99, 104	77, 75, 87	73, 65, 69
	0.05	92, 109, 85	87, 93, 86	97, 103, 91
Sugar beet roots	0.5	86, 92, 95	93, 107, 97	81, 82, 87
	0.05	100, 95, 115	95, 91, 86	117, 111, 107
Bovine fat	0.05	86	84	118
Bovine steak	0.05	102	88	112
Bovine milk	0.005	112	104	100
Lettuce	0.05	80	70	76
Cherry	0.05	94 (n = 2)	73 (n = 2)	91 $\pm$ 13 (n = 13)

Bayer Method 172 (Stanley and Strankowski, 1975) is a modification of Method 171. The oxidized product mixture is subjected to basic hydrolysis. The resulting sulfone phenols are transferred to acetone and derivatized with bis(trimethylsilyl)trifluoroacetamide (BSTFA). Extracts are analysed by GLC with a flame photometric detector in the sulfur mode. Recoveries are generally >80% and the limit of determination is 0.01 mg/kg (see method I340 below).

DFG analytical method 79-A-1 (Dräger, 1974) is a gas-chromatographic method applicable to apples, pears, soil, fat, meat, potatoes, maize, milk, beets, lettuce and white cabbage. It is very similar to method 171. Oily samples such as maize kernels are extracted with acetonitrile, as opposed to acetone/0.05 N HCl. For cabbage varieties, a thin-layer chromatographic separation of interfering constituents is required before silylation. Recoveries are stated to be generally above 87% at fortification levels of 0.05-0.5 mg/kg of each compound and at 0.005 mg/l for milk. Some specific recoveries are given in Table 21.

Table 21. Recoveries of methiocarb and metabolites from fortified samples by Method 79-A-1 (Dräger, 1974).

Sample	Fortification, mg/kg	Recovery, %		
		Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
Cauliflower, head	0.05	92	94	92
Cauliflower, stalks	0.05	99	96	96
Cauliflower, leaves	0.05	96	87	87
Apples	0.05	104	106	104
Pears	0.05	97	96	110
Strawberries	0.05	105	100	99
	0.5	104	96	100
Potatoes	0.05	78	73	76
Maize	0.05	88	72	82
Lettuce	0.05	108	105	109
Cabbage, white	0.1	97	109	100
Sugar beet, root	0.05	103	112	91
	0.5	91	83	99
Sugar beet, tops	0.05	95	97	89
	0.5	102	69	80

Bayer Method 00045, formerly I671 (Burger, 1988a,b) is used for the determination of methiocarb and degradation products in ground water. Benzanilide is added to the water sample (1 l) as an internal standard and the sample is passed through a solid phase extraction column (RP 18) at the rate of 1 ml/min. The column is dried with a nitrogen stream and eluted with acetonitrile/methanol (80/20). Numerous active ingredients, including methiocarb, are determined by TLC. Quantitative evaluation is by external standards, using peak heights measured by reflection densitometry. The reflectance curves of sample and standard peaks in each lane are plotted together in different colours at 6 measurement wavelengths. The recovery of methiocarb at 0.1 µg/l was 87.8 $\pm$ 4.0%, n = 5.

Bayer Method 00190 (Bachlechner, 1990) is an HPLC procedure for the determination of methiocarb, the sulfoxide and the sulfone individually in soil. A soil sample (50 g) is shaken with acetone/water (3/1, 300 ml) at pH 2.5 for 16 hours. The mixture is filtered and the filtrate is concentrated to an aqueous fraction of about 50 ml. The solution is cleaned up on solid phase extraction columns, using methylene chloride (200 ml) as eluant. The eluate is concentrated to dryness and dissolved in acetonitrile/water, pH 2.5. The extract is analysed by HPLC with a LiChrospher 60, RP-select B column, with post-column hydrolysis (0.05 N caustic soda, 90˚C) and derivatization (*o*-phthalaldehyde, 2-mercaptoethanol, borate buffer). The methylamine released from the hydrolysis of the carbamate reacts with the derivatizing agent to form 1-hydroxyethylthio)-2-methylisoindole, detected by fluorescence. Calibration is by external standards.

The practical limit of determination is 0.01 mg/kg per analyte and the limit of detection about 0.001 mg/kg per analyte. Recoveries were determined by fortifying three soils types separately with methiocarb, methiocarb sulfoxide and methiocarb sulfone at concentrations of about 0.01 to 0.15 mg/kg. The recoveries were 77-97%, n = 24, mean 87% $\pm$ 6% for methiocarb, 72-104%, n = 24, mean 90% $\pm$ 12% for methiocarb sulfone, and 80-114%, n = 24, mean 103% $\pm$ 11% for methiocarb sulfoxide.

Bayer Method 00014, formerly method I664 (Blass, 1988) is a variant of Method 00190 and is used for the determination of methiocarb, the sulfoxide and the sulfone in plant materials. Fatty substrates, such as nuts and artichokes (50 g) are extracted with acetonitrile and the extract is partitioned with hexane. The acetonitrile fraction is concentrated and the residue is partitioned between methylene chloride and water. The methylene chloride fraction is evaporated and the residue is cleaned up on Extrelut cartridges (fatty materials) or Florisil (artichokes). The analysis is completed as in Method 00190.

In modification M001 of Method 00014 (Blass, 1989d), fat-free plant materials such as cucumbers are macerated with dichloromethane and filtered. The filtrate is concentrated to dryness and cleaned up on an Extrelut cartridge as in Method 00014.

In a further modification, M002, of Method 00014 (Seym, 1991a) for residues of methiocarb and metabolites in the green foliage of cereals such as barley, samples (10 g) are macerated with dichloromethane (250 ml) and filtered. The filtrate is evaporated to dryness and the residue redissolved in hexane (5 ml). The extract is cleaned up on 1-g Bakerbond SPE silica gel cartridges that have been pre-washed with ethyl acetate and hexane. The analytes of interest are eluted with ethyl acetate. The analysis is completed as in Method 00014.

Modification M003 of Method 00014 (Seym, 1991b) is essentially M002 applied to wheat forage.

Modification M004 of Method 00014 (Seym, 1994a) is specific for strawberries, melons, tomatoes, leeks, lettuce and paprika. The method involves slight modifications to the extraction and clean-up. Plant material (50 g) is macerated with methylene chloride (200 ml). HCl (1 N, 5 ml) is also added for paprika, melon peel, lettuce and tomato. The mixtures are filtered and the filtrate is concentrated to an aqueous residue. Salt (15 g) is added (and for strawberry, leek and melon pulp only 1 N HCl, 3 ml), and the volume is adjusted with water to 50 ml. The solution is cleaned up on a Chem-Elut column. Extracts of leeks are further purified with a Florisil column. The analysis is completed as before.

Modification M006 of Method 00014 (Seym, 1998) was designed for leeks, red cabbage and white cabbage. The plant material (50 g) is blended with ethyl acetate (200 ml) and filtered. The filtrate is evaporated, mixed with 10% aqueous sodium chloride (18 ml) and 1.0 N HCl (2 ml) and cleaned up on a Chem-Elut CE 1020 column. The analytes are eluted with ethyl acetate/cyclohexane (85/15) and determined by HPLC. The limit of determination is 0.02 mg/kg and the limit of detection 0.006 mg/kg for each analyte.

Modification M007 of Method 00014 (Blass, 1998a) is specific for red and white cabbage. The cabbage (50 g) is macerated with acetonitrile (200 ml) and n-hexane (100 ml). The acetonitrile phase is evaporated to dryness and cleaned up on an Extrelut column or a Bakerbond SPE silica cartridge. The former is eluted with methylene chloride, the latter with acetonitrile.

Recoveries from fortified controls by Method 00014 and its modifications are shown in Table 22.

Table 22. Recoveries of methiocarb and its metabolites from fortified plant materials by HPLC Method 00014 and its modifications (Blass, 1988, 1989d, 1998a; Seym 1991a,b, 1994a, 1998).

Sample	Modification	Fortification, mg/kg	Recovery, %		
			Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
Artichoke		1.0	90	95	99
		0.04	82	89	96
Hazel nuts		1.0	96	97	96
		0.04	96	-	88
Tomato		1.0	88		-
		0.04	95	-	-
	M001	0.04	90	101	99
	M001	1.0	94	98	105
	M004	0.02	80	99	115
	M004	0.1	84	101	117
	M004	0.5	85		100
Strawberry		0.04	93	-	-
		1.0	98	-	-
	M001	0.04	82	90	94
	M001	1.0	91	94	95
	M004	0.05	80	90	114

Sample	Modification	Fortification, mg/kg	Recovery, %		
			Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
	M004	0.1	75 (68, 82)	95	124
	M004	0.5	74 (68, 79)	-	99
Strawberry jam	M001	0.04	92	87	96
	M001	1,0	94	88	95
Strawberry, canned	M001	0.04	79	81	93
	M001	1.0	90	85	90
Paprika		0.04	80	-	-
		1.0	92	-	-
	M001	0.04	91	120	94
	M001	1.0	87	113	97
	M004	0.02	76	97	106
	M004	0.1	74 (69, 79)	94	121
	M004	0.5	70 (61, 78)	89	113
Cucumber	M001	0.04	81	89	103
	M001	1.0	82	107	103
Wheat (summer), forage	M001	0.1	83	86	89
	M001	1.0	87	97	93
	M003	0.1	83	82	82
	M003	1.0	90	79	78
Wheat (summer), grain		0.04		103	
		1.0		101	
Wheat (summer), straw		0.04		102	
		1.0		122	
Barley (summer), grain		0.04	87	89	89
		1.0	93	93	99
Barley (summer), straw		0.1	79	83	87
		1.0	84	88	98
Barley (summer), forage	M002	0.1	87	93	78
	M002	1.0	82	84	80
Leek, stem	M004	0.02	90	109	106
		0.1	76	76	100
		0.5	76	-	97
	M006	0.02	82	105	100
		0.2	77	95	100
Melon, peel	M004	0.02	89	97	105
		0.1	75	97	125
		0.5	76	-	95
Melon, pulp	M004	0.02	88	96	101
		0.1	89	99	119
		0.5	93	89	108
Lettuce	M004	0.02	81	100	110
		0.1	80	101	130
		0.5	83	72	109
Cabbage, red	M006	0.02	83	99	99
		0.2	81	94	99
	M007	0.02	85	70	88
		0.10	100	79	91
		1.0	94	84	96
Cabbage, white	M006	0.02	75	87	85
		0.2	76	95	102
	M007	0.02	89	68 (63, 73)	84
		0.10	97	73	94

Sample	Modification	Fortification, mg/kg	Recovery, %		
			Methiocarb	Methiocarb sulfone	Methiocarb sulfoxide
		1.0	98	83	91

Method I340 is for the determination of methiocarb and five metabolites in poultry commodities (Delphia and Stanley, 1980). Ground tissue samples (50 g) are blended with acetonitrile (200 ml) and the extract partitioned with hexane (300 ml). Eggs are blended with acetone (200 ml) and the extract is partitioned with methylene chloride (300 ml) which is evaporated and the residue dissolved in acetonitrile and partitioned with hexane. The acetonitrile extract from tissues or eggs is evaporated to dryness and reconstituted in acetone, to which a precipitating solution of ammonium chloride is added. The mixture is filtered and the filtrate partitioned with methylene chloride. The solvent is changed to acetone and the analytes oxidized with permanganate. A methylene chloride extract of the oxidation mixture is changed to acetone and the mixture is hydrolysed with sodium hydroxide (2.5 N) at 60°C for 30 min. The product solution is acidified and extracted with methylene chloride. The analytes are derivatized with BSTFA (*N*,*O*-bis(trimethylsilyl)trifluoroacetamide) and determined by GLC on a 0.6 m x 2 mm i.d. column packed with 5% OV-225 with a flame photometric detector operated in the sulfur mode. Quantification is with external standards. The limit of determination is nominally 0.02 mg/kg. Some recoveries are shown in Table 23.

Table 23. Recoveries of methiocarb and metabolites from poultry fortified at 0.05 mg/kg, Method I340 (Delphia and Stanley, 1980).

Sample	Recovery, %					
	Methio-carb	Methiocarb sulfoxide	Methiocarb sulfone	*N*-hydroxymethyl-methiocarb	*N*-hydroxymethyl-methiocarb sulfoxide	*N*-hydroxymethyl-methiocarb sulfone
Muscle	88	78	76	84	78	116
Fat	92	96	76	100	120	92
Skin	88	76	82	80	96	96
Giblets	90	88	72	76	90	116
Eggs	98	120	94	76	78	102

Stability of pesticide residues in stored analytical samples

In a study of the stability of methiocarb and methiocarb sulfoxide in blueberries (Gronberg and Lemke, 1989) samples were fortified with radiolabelled methiocarb at 2.8 mg/kg or methiocarb sulfoxide at 3.3 mg/kg, stored in sealed jars at –23°C for 117-118 days, and analysed on day 0 and day 117 or 118. The samples were extracted with methanol and the extracts were radioanalysed, then analysed by HPLC with a radioactivity detector. A sample chromatogram was provided. About 1% loss of each compound occurred over the 117-118 days.

Summary information (giving fortification levels, storage periods and remaining percentages) was provided late in the JMPR evaluation process on the stability of methiocarb, methiocarb sulfoxide and methiocarb sulfone in beans and pods, bean vines, grapes, cabbage, rice grain, tomatoes, broccoli, Brussels sprouts and cauliflower (Anon., 1978). No details such as concurrent method recoveries (if any), sample chromatograms, exact temperatures of storage or procedures for fortification and analysis were provided. The information is shown in Table 24, but was insufficient to evaluate the results.

Table 24. Stability of methiocarb, methiocarb sulfoxide and methiocarb sulfone in plant commodities fortified separately with 1 mg/kg of each compound and stored at 0 to –10°C (Anon., 1978).

Commodity and analyte	Storage, days	Remaining, %
Methiocarb		
Beans with pods	0	100
	93	100
	216	100
	399	100
Grapes	0	100
	86	100
	209	88
	393	92
Bean vines	0	100
	88	84
	150	69
	369	83
Cabbage	0	100
	101	100
	182	100
	365	100
Cabbage	805	100
Rice grain	0	100
	95	67
	198	38
	360	58
Tomato	0	100
	90	100
	204	100
	389	100
Broccoli	804	79
Brussels sprouts	806	60
Cauliflower	805	100
Methiocarb sulfoxide		
Beans and pods	0	100
	93	94
	180	100
	403	88
Grapes	0	100
	86	100
	231	100
	397	93
Bean vines	0	100
	88	77
	150	82
	373	92
Cabbage	0	100
	101	88
	204	95
	370	95
Cabbage	805	54
Rice grain	0	100
	95	88
	190	80
	364	74
Tomato	0	100
	90	97
	204	09
	386	99
Broccoli	804	60
Brussels sprouts	806	52

Commodity and analyte	Storage, days	Remaining, %
Cauliflower	805	100
Methiocarb sulfone		
Beans with pods	0	100
	93	95
	180	90
	404	94
Grapes	0	100
	86	98
	231	93
	398	95
Bean vines	0	100
	88	92
	150	68
	374	74
Cabbage	0	100
	101	100
	204	100
	371	100
Cabbage	805	100
Rice grain	0	100
	95	83
	198	63
	365	62
Tomato	0	100
	90	100
	204	100
	386	100
Broccoli	804	34
Brussels sprouts	806	100
Cauliflower	805	100

Definition of the residue

The current residue definition for both plant and animal commodities is “sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb”. The Meeting concluded that it should be maintained.

USE PATTERN

Bayer AG provided labels or translated summaries of labels for uses of methiocarb in countries from which significant export of methiocarb-treated commodities is anticipated. Applications are generally foliar, as a seed treatment or granular to the soil. Additional information on uses was supplied by the governments of Australia, Germany, The Netherlands, Thailand and the UK. The registered uses are shown in Table 25.

Table 25. Registered uses of methiocarb.

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
All edible	UK	Pelleted bait. Draza 40 g/kg	0.22	+		1 or more	Broadcast; admixture at drilling	7	Slug and snail control. Admix with cereal, rye, clover, oilseed rape, brassica seeds
All edible	UK	Pelleted bait.	0.15			1 or more	Broadcast; admixture	7	Slug and snail control. Admix with

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		Draza 2 20 g/kg					at drilling		cereal, rye seed.
Almond	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Artichoke	Israel	WP, 500 g/kg	1.75			1	Foliar spray		
Asparagus	Italy	RB, 10 g/kg	0.1				Spreading	21	
Asparagus	Thailand	WP, 500 g/kg	0.75	750	0.05-0.1		Foliar	3	
Aubergine	Italy	WP, 500 g/kg			0.1		Foliar spray	21	Apply with normal volume pump
Aubergine	Italy	RB, 10 g/kg	0.1				Spreading	21	
Barley	Austria	RB 40 g/kg	0.12			2	Spreading	-	Slug and snail control
Barley	Belgium	RB, 40g/kg	0.12			2	Spreading		Slug and snail control
Barley	France	RB, 40 g/kg	0.12			1	Spreading		Slug and snail control
Barley	Germany	RB 20 g/kg	0.1			2	Post-sowing, up to stage 29. Even baiting		
Barley	Germany	GB, 40 g/kg	0.12			2	At drilling; post-sowing up to stage 29	7	
Barley	Ireland	RB, 40 g/kg	0.22			1	Spreading		Slug and snail control
Barley	Ireland	RB, 20 g/kg	0.15			1	Spreading		Slug and snail control
Barley	UK	RB, 40 g/kg	0.22				Admixture at planting. Spreading	7	Slug and snail control
Barley	UK	RB, 20 g/kg	0.15				Admixture at planting. Spreading		Slug and snail control
Bean	Italy	RB, 10 g/kg	0.1				Spreading	21	
Bean, green	Italy	RB, 10 g/kg	0.1				Spreading	21	
Bean	Spain	WP, 500g/kg			0.05-0.1		Foliar	7	
Beet	Belgium	FS, 500 g/l	10 ml/100, 000 seeds			1	Seed treatment		
Beet, red	Nether-lands	WP, 500 g/kg							
Berry	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast	7	
Cabbage	Austria	WP, 500 g/kg	0.25-0.50			1-2	Foliar spray	14	
Cabbage	Austria	RB, 40 g/kg	0.12			2	Spreading	14	Slug and snail control
Cabbage	Belgium	SC, 500 g/l	0.75			3	Foliar	14	
Cabbage	Belgium	RB, 40 g/kg	0.12			2	Spreading	14	Slug and snail control
Cabbage	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	Red, white, Savoy
Cabbage	Germany	GB, 40 g/kg	0.12			2	Baiting between plants	14	Red, white
Cabbage	Italy	WP, 500			0.1		Foliar	21	Apply with normal

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		g/kg							volume pump
Cabbage	Italy	RB, 10 g/kg	0.1				Spreading	21	
Cabbage	Nether-lands	WP, 500g/kg	1.5			1	Foliar	14	
Carrot	Italy	RB, 10 g/kg	0.1				Spreading	21	
Cauli-flower	Austria	RB, 40g/kg	0.12			2	Spreading	14	Slug and snail control
Cauli-flower	Belgium	RB, 40 g/kg	0.12			2	Spreading	14	Slug and snail control
Cauli-flower	Germany	RB, 20 g/kg; GB, 40 g/kg	0.1 0.12			2	Baiting between plants	14	
Cereals	Austria	RB, 40 g/kg	0.12			2	Spreading		
Cereals	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast	7	
Cereals	Sweden	RB, 40 g/kg							
Cereals	UK	RB, 20 g/kg RB, 40 g/kg	0.15 0.22				Admixture at seeding. Spreading. Aerial	7	
Chicory	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	Field and glasshouse
Clover	Italy	RB, 10 g/kg	0.1				Spreading	21	
Cotton	Spain	WP, 500 g/kg			0.05-0.1		Foliar	21	
Cotton	Thailand	WP, 500 g/kg	0.5	500	0.05-0.1		Foliar	21	
Cucumber	Belgium	SC, 500 g/l	0.6-0.8			1	Foliar	3	
Cucumber	Belgium	SC, 500 g/l	0. 4			1	Foliar	3	Glasshouse
Cucumber	Chile	WP, 500 g/kg	0.5				Foliar	15	
Cucumber	Greece	WP, 500 g/kg	0.8	500-800	0.1	2	Foliar	15	Field
Cucumber	Greece	WP, 500 g/kg	1.5	500-1500	0.1	2	Foliar	15	Glasshouse
Cucumber	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Cucumber	Nether-lands	SC, 500 g/l			0.05		Foliar	3	
Cucumber	Spain	WP, 500g/kg	0.5-1		0.05-0.1	2	Foliar	7	
Cucurbits	Italy	RB, 10 g/kg	0.1				Spreading	21	
Fruit	Austria	WP, 500 k/kg	1.5		0.5-1		Foliar	14	21-day grazing restriction
Gherkin	Belgium	SC, 500 g/l	0.0006-0.0008			1	Foliar	3	Glasshouse
Grapes	Australia	WP, 750 g/kg Mesurol 750			0.075-0.15	2	Cover spray	63	
Grapes	Chile	WP, 500 g/kg		1000-1500	0.05-0.075		Foliar		
Grapes	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Grapes	Italy	RB, 10 g/kg	0.1				Spreading	21	
Grapes	Spain	WP, 500 g/kg			0.05-0.1		Foliar, before		Table and wine

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
							flowering		
Grapes	Thailand	WP, 500 g/kg	2.5	2500	0.05-0.1		Foliar, 5-7 day interval	21	
Hazel nut	Spain	WP, 500 g/kg	5 g ai/tree trunk; -		-; 0.05-0.1		Tree trunk paint; Foliar	21	
Hazel nut	Turkey	WP, 500 g/kg	0.6		0.25-0.375	1	Foliar	90	
Hops	Spain	WP, 500 g/kg			0.05-0.1		Foliar	21	
Leek	Belgium	SC, 500 g/l	0.75			2-3	Foliar	21	
Leek	Nether-lands	SC, 500 g/l	0.5-0.75			3	Foliar	14	
Lettuce	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	Head, Cos, Leaf. Field and glasshouse
Lettuce, head	Germany	GB, 40 g/kg	0.12			2	Baiting between plants	14	Field and glasshouse
Maize	Austria	WP, 500 g/kg. FS, 500 g/l	0.50 kg ai/dt (1 kg formul-ation/100 kg seed)			1	Seed treatment	-	
Maize	Belgium	WP, 500 g/l	0.50 kg/dt			1	Seed treatment		
Maize	Germany	FS 500 g/l	1 L/100 kg seed			1	Seed treatment	-	
Maize	Italy	WP, 500 g/kg	0.5 kg ai/100 kg seed				Seed treatment		
Maize	Nether-lands	SC, 500 g/l	0.5 kg ai/100 kg seed			1	Seed dressing		
Melon	Italy	WP, 500 g.kg	0.8-1.0 (calcu-lated)		0.1	2	Foliar	7	
Melon	Nether-lands	SC, 500 g/l			0.05		Foliar	3	
Melon	Portugal	WP, 500 g/kg	0.8-1 (calcu-lated)		0.1	2	Foliar	7	Field and glasshouse
Nectarine	Chile	WP, 500 g/kg	0.5-1.12	1000-1500	0.05-0.075		Foliar		
Nectarine	Spain	WP, 500 g/kg			0.05-0.1		Foliar, before flowering		
Oats	Germany	RB 20 k/kg	0.1			2	Post sowing up to stage 29. Even baiting		
Oats	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Oilseed crops	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast to ground	7	
Oranges	Australia	WP, 750 g/kg Mesurol 750			0.075		Cover spray	42	
Orchards	Australia	GB, 20 g/kg	0.11; 0.22-				Broadcast to ground	7	

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		Mesurol	0.44						
Pastures	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast to ground	7	
Peach	Spain	WP, 500 g/kg			0.05-0.1		Foliar, before flowering		
Peas	Germany	FS, 500g/l	0.5 L/100 kg seed				Seed treatment		
Peas	Italy	RB, 10 g/kg	0.1				Spreading	21	
Peas	Nether-lands	FS, 500 g/l	0.25 kg/100 kg seed			1	Seed treatment		
Peas	Spain	WP, 500 g/kg			0.05-0.1		Foliar	7	
Pepper, bell	Chile	WP, 500 g/kg	0.6	600-800	0.05-0.075		Foliar	14	
Pepper	Italy	RB, 10g/kg	0.1				Spreading	21	
Pepper	Portugal	WP, 500 g/kg	0.8-1 (calcu-lated)		0.1	2	Foliar	14	Field and glasshouse
Pepper	Spain	WP, 500 g/kg	0.4-1		0.05-0.10	3	Foliar	7	
Pepper. Chili	Thai-land	WP, 500 g/kg	0.5	500	0.05-0.1		Foliar, 7-10 day interval	21	
Pome fruit	Italy	WP, 500 g/kg			0.1		foliar	21	Apply with normal volume pump
Pome fruit	Italy	RB, 10 g/kg	0.1				Spreading	21	
Potato	Ireland	RB, 40 g/kg	0.22			3	Spreading		Slug control
Potato	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Potato	Italy	RB, 10 g/kg	0.1				Spreading	21	
Potato	UK	RB, 40 g/kg	0.22			3	Spreading		
Radish	Italy	RB, 10 g/kg	0.1				Spreading	21	
Rape	Austria	RB 40g/kg	0.12			2	Spreading		
Rape	Belgium	RB, 40 g/kg	0.12			2	Spreading		
Rape	France	WP, 500 g/kg	2.5 kg ai/q seeds			1	Seed treatment		
Rape	France	WP, 500 g/kg			0.1		Foliar	15/	
Rape	France	RB, 40 g/kg	0.12			1	Spreading	15	
Rape	Germany	RB, 20 k/kg	0.1			2	Post-sowing up to stage 29-30. Even baiting	15	Slug and snail control
Rape	Nether-lands	WP, 500 g/kg	0.5			1	Foliar		
Rape	Sweden	RB, 40 g/kg							Last application at 4-5 leaves stage
Rape	UK	RB, 40 g/kg	0.22			2	Spreading		Slug and snail control
Rape	UK	RB, 20 g/kg	0.11			1	Spreading	7	Slug and snail control
Rye	Germany	RB, 20 g/kg; GB, 40	0.1 0.12			2	Post sowing up to stage 29.		

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		g/kg					Even baiting		
Rye	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Scarole	Germany	RB, 20 g/kg	0.1			2	Baiting between plants	14	
Spinach	Germany	RB, 20 g/kg GB, 40 g/kg	0.1 0.12			2	Baiting between plants	14	Field and glasshouse. Field only for GB
Stone fruit	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Sugar beet	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Sugar beet	Italy	RB, 10 g/kg	0.1				Spreading	21	
Stone fruit	Italy	RB, 10g/kg	0.1				Spreading	21	
Sugar beet	Italy	WP, 500 g/kg	0.5 kg ai/100 kg seed				Seed treatment		
Sugar beet	Nether lands	WP, 500 g/kg							
Straw-berry	Austria	RB, 40 g/kg	0.12			2	Spreading		
Straw-berry	Belgium	RB, 40 g/kg	0.20			2	Spreading		Slug and snail control
Straw-berry	Finland	SC, 500 g/l	3		0.15		Foliar after harvest		
Straw-berry	Germany	RB, 20 g/kg GB, 40 g/kg	0.1 0.12			2	Baiting between plants	14	
Straw-berry	Ireland	RB, 40 g/kg	0.22			1	Spreading		Slug and snail control
Straw-berry	Ireland	RB, 20 g/kg	0.10			1	Spreading		Slug and snail control
Straw-berry	Italy	WP, 500 g/kg	0.7-1.2 (calcu-lated)		0.1	1	Foliar	21	
Straw-berry	Italy	RB, 40 g/kg	0.12-0.2			2	Spreading	14	Slug and snail control
Straw-berry	Italy	RB, 10 g/kg	0.1				Spreading	21	
Straw-berry	Portugal	WP, 500 g/kg	0.8		0.1	2	Foliar	7	Field and glasshouse
Straw-berry	Spain	WP, 500 g/kg	0.4-1		0.05-0.1	2	Foliar	15	Field and glasshouse
Straw-berry	Sweden	RB, 40g/kg	0.2			1	Spreading		Slug and snail control
Straw-berry	UK	RB, 40 g/kg	0.22			1	Spreading		Slug and snail control
Straw-berry	UK	RB, 20 g/kg	0.10			2	Spreading	7	Slug and snail control
Sun-flowers	Australia	GB, 20 g/kg Mesurol	0.05; 10 pellets/ m^2				Broadcast to ground	7	
Tomato	Chile	WP, 500 g/kg	0.6	600-800	0.05-0.075		Foliar	15	
Tomato	Italy	RB, 10 g/kg	0.1				Spreading	21	
Tomato	Portugal	WP, 500 g/kg	0.8-1 (calcu-lated)		0.1	2	Foliar	7	Field and glasshouse
Tomato	Spain	WP, 500	0.5-1		0.05-0.1	2	Foliar	7	Field and

Crop	Country	Form	Application					PHI, days	Comments
			Rate, kg ai/ha	Rate, l/ha	Spray conc., kg ai/hl	No.	Method		
		g/kg							glasshouse
Triticale	Germany	RB, 20 g/kg	0.1				Post sowing up to stage 29. Even baiting		
Triticale	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Vegetables	Austria	WP, 500 g/kg	1.5	300-600	0.5-1		Foliar	14	21-day grazing restriction
Vegetables	Austria	RP, 40 g/kg	0.12			2	Spreading		
Vegetables	Australia	GB, 20 g/kg Mesurol	0.11; 0.22-0.44				Broadcast to ground	7	
Vegetables	Germany	RB, 20 g/kg	0.1			2	Spreading	14	
Vegeta-bles, leaf	Italy	RB, 10 g/kg	0.1				Spreading	21	
Water-melon	Italy	WP, 500 g/kg			0.1		Foliar	21	Apply with normal volume pump
Water-melon	Thailand	WP. 500 g/kg	0.5	500	0.05-0.1		Foliar, 5-7 day interval	10	
Wheat	Belgium	GB, 40 g/kg	0.12				Spreading	1-4	Slug and snail control
Wheat	France	RB, 40 g/kg	0.12			1	Spreading		Slug and snail control
Wheat	Germany	RB, 20 g/kg	0.1			2	Post sowing up to stage 29. Even baiting		
Wheat	Germany	GB, 40 g/kg	0.12			2	At drilling; post sowing up to stage 29		
Wheat	Portugal	WP, 500 g/kg	3			1	Foliar, at milk growth stage	28	Bird repellent
Zucchini	Chile	WP, 500 g/kg	0.6	600-800	0.05-0.075		Foliar	15	

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of the residue trials are shown in Tables 26-41. The trials were reported in sufficient detail, with acceptable analytical information, unless otherwise noted. Double underlined residue values are from treatments according to GAP and are valid for use in the estimation of maximum residue levels and STMRs. The commodities covered by the Tables are as follows.

Table number	Commodity
26	Potato
27	Leek
28	Cabbage
29	Cabbage
30	Cauliflower
31	Peas
32	Pepper
33	Tomato

Table number	Commodity
34	Cucumber
35	Melon
36	Strawberry
37	Wheat
38	Barley
39	Maize
40	Hazelnuts
41	Rape

Information on supervised trials was supplied by Bayer AG.

Potatoes. Trials were reported from the UK (Seym and Walz-Tylla, 1993a). GAP in the UK and Ireland is up to three applications of a granular formulation at 0.22 kg ai/ha. No PHI is specified. Trials were conducted with Draza 4 RB in the UK in 1991. The details are shown in Table 26. Samples were stored frozen for 14 months before analysis.

Table 26. Residues of methiocarb and its metabolites in or on potatoes in the UK following application of methiocarb RB, 40 g/kg.

Location/ Year/ Ref. no.	Rate, kg ai/ha	No. of applications/ time of last application	PHI, days	Methiocarb/ sulfoxide/ sulfone, mg/kg	Method of analysis	Fortified control recoveries	
						Fort., mg/kg	Recovery, %
Thurston, Suffolk/ 1991/ 2038/91	0.22	3/ Starting of senescence, mature tubers	18	<0.02 <0.02 <0.02	00014/ M002/ E008	Methiocarb: 0.02 0.2 1.0 Sulfone: 0.02 0.1 1.0 Sulfoxide: 0.02 0.2 1.0	 72 74 66 88 68 74 66 88 97
Deal, Kent/ 1991/ 2038-91	0.22	3/ Starting of senescence, mature tubers	20	<0.02 <0.02 <0.02			

Leeks. A total of 11 field trials were reported from France and The Netherlands (Seym, 1994b, 1995a; Walz-Tylla and Deissler, 1998b). GAP for France was not reported. In The Netherlands up to 2 foliar applications of an SC formulation, 500 g/l, may be made at rates of 0.5-0.75 kg ai/ha, with a 14-day PHI. Similar GAP exists for Belgium, but the PHI is 21 days. GAP of The Netherlands was applied to the trials in France. The pertinent conditions and results are shown in Table 27. The residues were determined by HPLC Method 00014, modification M004. Recoveries in the 1993 trials from fortified controls (13 determinations, 0.02-0.5 mg/kg) were 75-93% for methiocarb, 52-112% for methiocarb sulfone (67-112% at or above 0.2 mg/kg) and 86-108% for methiocarb sulfoxide. In the 1994 trials recoveries of methiocarb were 57-87% (n = 6), of methiocarb sulfone 86-108% (n = 6) and of methiocarb sulfoxide 98-101% (n =6). Concurrent recoveries in the 1996 French field trials at fortification levels of 0.02-0.5 mg/kg (7 determinations) were 75-94% for methiocarb, 93-105% for methiocarb sulfone, and 94-112% for methiocarb sulfoxide. The limit of determination was 0.02 mg/kg per analyte. Control samples showed no residues (<0.02 mg/kg). Samples were stored frozen for 1-12 months before analysis.

Table 27. Residues of methiocarb and its metabolites in or on leeks from foliar application of methiocarb in France and The Netherlands (Seym, 1994b, 1995a; Walz-Tylla and Deissler, 1998b)

Location/ Year/ Variety	Form	Rate, kg ai/ha	Vol., l/ha	No./ interval, days	PHI, days	Methio-carb, mg/kg	Sulfone, mg/kg	Sulfoxide, mg/kg	Report no.
Bouafle, France/ 1993	Mesurol WP, 500 g/kg	0.75	280	3/14, 24	0 7 14 21	4.1 0.42 0.07 0.03	0.05 0.03 0.03 <0.02	0.94 0.32 0.15 0.06	2085/93
Ecquevilly, France/ 1993	Mesurol WP, 500 g/kg	0.75	280	3/14,24	0 7 14 21	4.2 0.37 0.10 0.04	0.06 0.05 0.03 <0.02	0.45 0.24 0.16 0.06	2085/93
Ecquevilly, France/1994/ Nepal	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 7 14 21	2.8 0.24 0.05 <0.02	0.05 0.06 0.02 <0.02	0.29 0.37 0.11 0.07	2070/94
Ecquevilly, France/ 1994/ Arkansas	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 21	2.4 0.04	0.04 <0.02	0.37 0.10	2070/94
Sorgues, France/1996	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 7 14 21 28	3.3 0.51 0.22 0.09 0.05	0.02 0.04 <0.02 <0.02 <0.02	0.47 0.34 0.17 0.09 0.06	2156/96
Lombez, France/ 1996 (2 replicates)	Mesurol WP, 500 g/kg	0.75	280	3/14,13-14	0 21	3.5; 2.7 0.13;0.16 (0.14)	0.04;0.05 <0.02;0.03 (0.03)	0.52;0.46 0.09;0.15 (0.12)	2156/96
Bonnetan, France/1996	Mesurol WP, 500 g/kg	0.75	280	3/14,14	0 7 14 21 28	5.0 0.51 0.13 0.07 0.02	0.07 0.08 0.05 0.03 <0.02	0.57 0.37 0.12 0.08 0.04	2156/96
PT Toll-ebeek, NL/ 1993	Mesurol SC, 500g/l	0.75	1000	3/11,9	0 7 14 21	2.0 0.12 0.03 <0.02	0.03 0.02 <0.02 <0.02	0.39 0.23 0.05 0.03	2085/93
PE Drot-erop-slagen, NL/1993	Mesurol SC, 500 g/l	0.75	1000	3/11,9	0 7 14 21	2.2 0.07 <0.02 <0.02	0.04 <0.02 <0.02 <0.02	0.38 0.10 0.02 <0.02	2085/93
AA Dongen, NL/1994	Mesurol SC, 500 g/l	0.75	1000	3/10,10	0 3 7 14 21	2.6 0.26 0.10 0.03 <0.02	<.02 0.04 <0.02 <0.02 <0.02	0.17 0.20 0.10 <0.02 <0.02	2070/94
RB Deurne, NL/1994	Mesurol SC, 500 g/l	0.75	1000	3/10,10	0 21	1.1 0.02	0.05 <0.02	0.61 <0.02	2070/94

Cabbages. Field trials were reported from Austria, Belgium, Germany and The Netherlands (Bayer AG, 1978, 1980c; Blass, 1998b; Walz-Tylla, 1998). GAP for Belgium is 3 foliar applications at 0.75 kg ai/ha of an SC formulation or 2 applications by spreading on the ground of an RB formulation at 0.12 kg ai/ha. The PHI is 14 days. GAP for Germany is 2 applications of RB formulations, baiting between plants, at 0.12 kg ai/ha, 14 day PHI. GAP for The Netherlands is one foliar application of a WP formulation at 1.5 kg ai/ha, 14 day PHI. GAP for Belgium for the SC formulation was applied to evaluate the trials in The

Netherlands and some of those in Germany. The trial conditions and results are shown in Tables 28 and 29. Samples were stored frozen for 1-10 months before analysis.

Table 28. Residues of methiocarb and its metabolites in or on cabbages from foliar application or ground application of baits (Bayer, 1978, 1980c).

Location/ Year/ species	Form.	Rate, kg ai/ha	Vol., l/ha	No./interval, days	PHI, days	Residue, mg/kg (methiocarb + sulfoxide + sulfone)	Report no.
Pfalz, Germany/ 1978/Savoy	4% RB	0.12	-	1	0 4 7 14 21	0.34 0.66 <0.05 <u>≤0.05</u> -	2103-78
Monheim, Germany/ 1978/Savoy	4% RB	0.12	-	1	<u>0</u> 4 7 14 21	<u>≤0.05</u> - - - -	2104-78
Bursheid, Germany/ 1978/Savoy	4% RB	0.12	-	1	<u>0</u>	<u>≤0.05</u>	2105-78
Pfalz, Germany/ 1980/White	4% RB	0.12	-	2/14	0 4 7 14 28	0.89 0.23 <0.05 <u>≤0.05</u> <0.05	2107-80
Bursheid, Germany/ 1980/White	4% RB	0.12	-	2/14	0 4 7 14 28	0.06 <0.05 <0.05 <u>≤0.05</u> <0.05	2108-80
Monheim, Germany/ 1980/White	4% RB	0.12	-	2/14	0 4 7 14 28	0.09 0.24 0.09 <u>≤0.05</u> <0.05	2109-80
Niederoster-reich, Austria/ 1981/White	WP 50%	1.5	600	1	0 14 21 28 35	0.52 0.09 0.05 <0.05 <0.05	

Table 29. Residues of methiocarb and its metabolites in or on cabbages (Walz-Tylla, 1998; Blass, 1998b).

Location /year /species	Application				PHI, days	Methio-carb, mg/kg	Methio-carb sulfone, mg/kg	Methio-carb sulf-oxide, mg/kg	Report no.
	Form.	kg ai/ha	Vol., l/ha	No. per interval, days					
Luttelgeest, NL/1996 /Round	Mesurol SC, 500 g/l	0.75	500	3/16,14	0 7 14 21	0.11 <0.02 <u>≤0.02</u> <0.02	<0.02 <0.02 <u>≤0.02</u> <0.02	0.10 0.08 <u>0.03</u> 0.03	2157/96
Luttelgeest, NL/1996 /Red	Mesurol SC, 500 g/l	0.75	500	3/16,14	0 7 14 21	0.09 <0.02 <u>≤0.02</u> <0.02	<0.02 <0.02 <u>≤0.02</u> <0.02	0.05 0.04 <u>0.03</u> 0.02	2157/96
Echteld, NL/1996 /Red	Mesurol SC, 500 g/l	0.75	500	3/14, 14	0 7 14 21	0.05 <0.02 <u>≤0.02</u> <0.02	<0.02 <0.02 <u>≤0.02</u> <0.02	0.06 0.03 <u>0.02</u> <0.02	2157/96

Location /year /species	Application				PHI, days	Methio-carb, mg/kg	Methio-carb sulfone, mg/kg	Methio-carb sulf-oxide, mg/kg	Report no.
	Form.	kg ai/ha	Vol., l/ha	No. per interval, days					
Brielle, NL/1996 /Round	Mesurol SC, 500 g/l	0.75	500	3/14,14	0 7 14 21	0.10 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.12 0.08 0.03 <0.02	2157/96
Laacherhof Germany/ 1997/ Round	Mesurol SC, 500 g/l	0.75	500	3/14,14	0 7 14 21	0.564 0.04 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.10 0.05 <0.02 <0.02	2004/97
Laacherhof Germany/ 1997/Red	Mesurol SC, 500 g/l	0.75	500	3/14,14	0 7 14 21	0.81 0.10 0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.15 0.10 0.03 <0.02	2004/97
Poederlee, Belgium/ 1997/ Round	Mesurol SC, 500 g/l	0.70-0.75	463-500	3/14,17	0 6 14 20	0.15 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.04 <0.02 <0.02 <0.02	2004/97
Poederlee, Belgium/ 1997/Red	Mesurol SC, 500 g/l	0.75	500	3/14,17	0 6 14 20	0.19 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	0.04 0.03 <0.02 <0.02	2004/97

NL = Netherlands
Recoveries in the NL trials (0.02-0.2 mg/kg, n=12) were 53-86% for methiocarb, 85-102% for methiocarb sulfone, and 85-134% for methiocarb sulfoxide. In the 1997 trials in Germany and Belgium (0.02-1.0 mg/kg, n=28), 78-118% for methiocarb, 73-126% for methiocarb sulfoxide, and 63-107% for methiocarb sulfone.

Cauliflower. Four trials in Germany were reported as summaries (Bayer AG, 1980d, 1981). GAP for Germany is 2 applications of an RB formulation to the ground at 0.12 kg ai/ha, with a 14-day PHI. Similar GAP exists in Austria and Belgium. The results of the trials are shown in Table 30. Analyses were by Method 171.

Table 30. Residues of methiocarb and its metabolites in cauliflowers in Germany (Bayer AG, 1980d, 1981).

Location/year	Application			PHI, days	Methiocarb + methiocarb sulfoxide + methiocarb sulfone, mg/kg	Report no.
	Form	kg ai/ha	No/interval, days			
Pfalz, 1980	4% GB	0.12		0 4 7 14	0.97 0.1 0.06 <0.05	2110-80 2111-80 2112-80
Burscheid, 1980	4% GB	0.12	2/14	14 (leaf) 28	<0.05 <0.05	
Laacherhof, 1980	4% GB	0.12	2/16	0 4 7 14 28	0.96 0.24 0.12 <0.05 <0.05	
Laacherhof, 1981	4% GB	0.12	2/11	0 4 7 14 28	<0.05 <0.05 <0.05 <0.05 <0.05	2105-81

Artichokes. Two trials were reported from Italy (Bayer AG, 1988). No GAP is reported for Italy, but GAP for Israel is one foliar application of a WP formulation at 1.75 kg ai/ha, with no specified PHI. The trials

were conducted at Brindisi in 1987 and 1988 (duplicate plots) with a 50% WP formulation applied twice at a rate of 1.0 kg ai/ha. Residues were <0.04 mg/kg on the flower heads at a PHI of 21 days. At 0 days the residues were 2.7 mg/kg in 1987 and 2.9 mg/kg and 1.2 mg/kg in 1988.

Peas. Eight trials were reported from Germany (Bayer AG, 1985, 1986). GAP for Germany is a seed treatment at 0.5 l per 100 kg of seed of a 500 g/l FS formulation. The formulation was applied in the field at planting. The results are shown in Table 31. The samples were stored from <1-12 months before analysis.

Table 31. Residues of methiocarb and its metabolites in trials on peas in Germany (Bayer AG, 1985, 1986).

Location/year	Application rate (kg ai/ha)	PHI, days	Sample	Residue,[1] mg/kg	Report no.
Klein-Niedesheim, 1985	0.90	65 84 65	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2103-85
Worms-Heppenheim, 1985	0.85	69 86 69	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2102-85
Laacherhof, 1985	1.1	63 99 63	Pea and pod Dry pea Vine	<0.05 <0.05 <0.05	2101-85
Versuchsgut Höfchen, 1985	1.1	97 132 97	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2100-85
Laacherhof, 1986	0.90	58 83	Vine Pea	<0.05 <0.05	2113-86
Versuchsgut Höfchen, 1986	0.90	62 91 62	Pea with pod Pea Vine	<0.05 <0.05 <0.05	2112-86
Worms-Heppenheim, 1986	0.85	63 75 63	Pea and pod Pea Vine	<0.05 <0.05 <0.05	2111-86
Klein-Niedesheim, 1986	0.85	51 65 51 65 89	Pea and pod Pea Vine Straw Dry pea	0.07 0.08 0.04 0.08 0.06	2110-86

[1]Combined residues of methiocarb, methiocarb sulfone and methiocarb sulfoxide

Peppers. Five trials were reported from Spain (Bayer AG, 1989c, 1992f; Seym, 1997; Seym and Walz-Tylla, 1993b) and 2 glasshouse trials from Portugal (Seym, 1997). GAP is similar in both countries, 3 applications in Spain and 2 applications in Portugal at 1 kg ai/ha, with a 7-day PHI in Spain and a 14-day PHI in Portugal. Portugal's GAP includes field and glasshouse use. The formulation is 500 g/kg WP. Analyses were by HPLC Method 00014, E002, but in some cases only the total residue was reported. The results are shown in Table 32. Samples were stored for 1-6 months before analysis. The shorter PHI of Spain was applied to the trials in Portugal in determining which residue values were appropriate for estimating an STMR.

Table 32. Residues of methiocarb and its metabolites in peppers.

Location/ Year	Application			PHI, days	Methiocarb, mg/kg	Methiocarb sulfone mg/kg	Methiocarb sulfoxide mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval days					
Almeria, Spain/1988 Variety Ator	1.0	1000	3/14, 14	0 5 10 15	0.71 (total) 0.48 0.46 0.92			0720-88
Almeria, Spain/1988/ Variety Clovis	1.0	1000	3/14, 14	0 5 10 15	0.81 (total) 0.84 0.55 0.49			0719-88
Murcia, Spain/1990 Variety Gedeon (replicate plots)	1.0	1000	2/14	0 3 7 14	0.92; 0.60; 0.86 1.0; 0.49; 0.89 0.96; 0.78; 0.81 0.68; 0.49; 0.60	<0.04 <0.04 <0.04 <0.04	0.33;0.37;0.39 0.49;0.44;0.42 0.37;0.56;0.44 0.33;0.36;0.38	0194-90
Malgrat, Spain/1991 (see processing)	1.0 1.5	1000 1500	2/14	0 3 7 10	2.4 1.3 0.82 0.28	<0.04 <0.04 <0.04 <0.04	0.32 0.33 0.38 0.22	2103/91
Viladecans, Spain/1991 (see processing)	1.0	1000	2/14	0 3 7 10	2.2 1.2 1.1 0.15	<0.04 <0.04 <0.04 <0.04	0.20 0.25 0.43 0.14	2103/91
Figueiras, Portugal (glasshouse)/ 1993	1.0 1.2 1.0	1000 1155 1000	3/7, 9	0 3 7 14 28	0.57 0.33 0.36 0.22 0.17	<0.02 <0.02 <0.02 <0.02 <0.02	0.34 0.24 0.33 0.27 0.13	2087/93
Bordinheira, Portugal (glasshouse)/ 1994 (see processing)	1.2 1.3 1.3	1173 1306 1306	3/7, 9	0 3 5 7 14 28	0.18 0.08 0.09 0.13 0.03 0.03	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.05 0.06 0.08 0.10 0.03 0.24	2087/93

Method recoveries in Portugal (0.02-0.5 mg/kg, n = 11) were 61-81% for methiocarb, 85-99% for methiocarb sulfone, and 98-124% for methiocarb sulfoxide.

Tomatoes. Eight trials were reported from Southern Europe, 1 in Portugal and 7 in Spain (Bayer AG, 1989a,b, 1992a-c; Seym, 1997). GAP for Portugal and Spain is identical, 2 foliar applications of a WP 500 g/kg formulation at 0.1 kg ai/ha per application with a 7-day PHI. Both glasshouse and field applications are specified. The results are shown in Table 33. Samples were stored from 1 month to 16 months before analysis.

Table 33. Residues of methiocarb and its metabolites in tomatoes (Bayer, 1989a,b, 1992a-c; Seym, 1997).

Location/ Year Variety	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
Almeria, Spain/1988/ Caruso	1.0	1500	3/14, 14	0 5 10 15	0.18 (total) 0.13 0.12 0.17			0721-88
Almeria, Spain/1988/ Buffalo	1.0	1500	3/14,14	0 5 10 15	0.14 (total) 0.13 0.08 0.17			0722-88
Viladecans, Spain/ 1990	1.0	1000	2/15	0 3 7	0.23 0.18 0.06	<0.04 <0.04 <0.04	0.10 <0.04 0.05	0210-90

Location/ Year Variety	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
				15	<0.04	<0.04	<0.04	
Malgrat de Mar, Spain/1990	1.0	1000	2/15	0 3 7 15	0.42 <0.04 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.13 <0.04 <u>≤0.04</u> <0.04	0211-90
Matar, Spain/1990	1.0	1000	2/15	0 3 7 15	0.35 0.32 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.13 <0.04 <u>≤0.04</u> <0.04	0212-90
Santarem, Portugal/ 1993/ glasshouse	1.0 1.1	1000	2/15	0 3 5 7 14 21	0.99 0.97 0.72 <u>0.59</u> 0.34 0.26	<0.02 <0.02 <0.02 <u>≤0.02</u> <0.02 <0.02	0.23 0.28 0.25 <u>0.22</u> 0.26 0.08	2087/93 #0438-93
Viladecans, Spain/1993/ glasshouse	1.2 1.4 1.4	1209 1416 1416	3/13,13	0 3 5 7 14	0.48 0.30 0.13 0.13 0.08	<0.02 <0.02 <0.02 <0.02 <0.02	0.09 0.12 0.07 0.10 0.10	2087/93 #0431-93
Vicar, Spain/1993/ glasshouse	1.5 1.4 1.5	1500 1407 1500	3/12,14	0 7 14	0.70 0.45 0.42	<0.02 <0.02 <0.02	0.17 0.13 0.17	2087/93 #0440-93

Method recoveries in the 1993 greenhouse trials in Spain and Portugal (0.02-0.2 mg/kg, n=7) were 81-93% for methiocarb, 87-101% for methiocarb sulfone, and 99-112% for methiocarb sulfoxide

<u>Cucumbers</u>. Two trials were reported from Spain (Bayer AG, 1992e) and four glasshouse trials from France (Seym and Heinemann, 1995). An additional report on trials in The Netherlands was withdrawn by Bayer AG. No GAP was reported for France. In Spain, a WP formulation may be applied as a foliar spray at 1 kg ai/ha, two applications maximum, PHI 7 days. Italy has a similar application, but no maximum number of applications and a 21-day PHI. Samples were analysed by HPLC Method 00014, M001. The results are shown in Table 34. Samples were stored from 1-6 months before analysis.

Table 34. Residues of methiocarb and its metabolites in or on cucumbers.

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
Viladecans, Spain/ 1990	1.0	1000	2/15	0 3 7 15	0.11 0.08 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.10 0.08 <u><0.04</u> <0.04	0217-90
Matar, Spain/1990	1.0	1000	2/15	0 3 7 15	0.57 0.22 <u>≤0.04</u> <0.04	<0.04 <0.04 <u>≤0.04</u> <0.04	0.18 0.06 <u>≤0.04</u> <0.04	0215-90
Montfavet, France/1994 glasshouse	0.80	1066	1	0 3 7	0.23 0.13 <u>≤0.02</u>	<0.02 0.03 <u>≤0.02</u>	0.06 0.10 <u>0.05</u>	2036/94 #0144-94
Montfavet/, France/1994 glasshouse	0.79	1055	1	0 3 7	0.17 0.14 <u>0.03</u>	<0.02 0.02 <u>≤0.02</u>	0.05 0.10 <u>0.07</u>	2036/94 #0145-94
Bellegarde, France/1994 glasshouse	0.86	1153	1	0 3 7	0.17 0.09 <u>0.02</u>	<0.02 <0.02 <u>≤0.02</u>	0.04 0.10 <u>0.09</u>	2036/94 #0146-94

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No./interval, days					
Bellegarde, France/1994 glasshouse	0.86	1145	1	0 3 7	0.15 0.04 <0.02	<0.02 <0.02 <0.02	0.04 0.07 0.07	2036/94 #0147-94

[1]In the French trials concurrent recoveries (0.02-0.2 mg/kg, n = 6) were 76-95% for methiocarb, 93-103% for methiocarb sulfone and 106-114% for methiocarb sulfoxide.

Melons. Seven trials on melons were reported from Southern Europe, 3 in France (Walz-Tylla and Deissler, 1998a), 2 glasshouse in Portugal and 2 in Spain (Seym, 1997). GAP was not reported for France or Spain. In Portugal and Italy a WP formulation may be applied twice at a maximum rate of 1 kg ai/ha with a 7-day PHI. The samples were analysed by HPLC Method 00014, M004. The results are shown in Table 35. The samples were stored frozen for 11-13 months before analysis. The residues in whole melons were calculated from the residues determined in the pulp and peel in those cases where whole melons were not analysed.

Table 35. Residues of methiocarb and its metabolites in or on melons (Walz-Tylla and Deissler, 1998; Seym, 1997).

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No. per interval, days					
Santeren, Portugal/ 1993	1.0	1000	2/18	0 pulp 3 7 14 28 0 peel 3 7 14 28 7 whole (2.08 kg whole, 1.47 kg pulp, 0.61 kg peel)	0.07 <0.02 <0.02 <0.02 <0.02 1.70 0.74 0.96 0.41 0.19 0.29	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.12 0.05 0.06 0.04 <0.02 1.20 0.64 0.55 0.32 0.16 0.20	2087/93 #0436-93
Alenquer, Portugal/ 1993	1.0	1000	2/14	0 pulp 3 5 7 14 28 0 peel 3 5 7 14 28 7 whole (4.14 kg whole, 3.46 kg pulp, 0.68 kg peel)	<0.02 0.07 <0.02 <0.02 <0.02 <0.02 0.39 1.70 0.68 0.63 0.33 0.15 0.11	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02 <0.02	0.03 0.08 <0.02 0.06 0.04 <0.02 0.46 0.74 0.33 0.59 0.25 0.17 0.15	2087/93 #0437-93
Santa Olive, Spain/ 1993	1.0	1000	2/14	0 pulp 3 5 7 0 peel	0.02 <0.02 <0.02 <0.02 1.20	<0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02 0.40	2087/93 #0442-93

Location/ Year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	kg ai/ha	Vol., l/ha	No. per interval, days					
				3 5 7 7 whole (26.1 kg whole, 18.4 kg pulp, 7.74 kg peel)	0.26 0.38 0.29 0.09	<0.02 <0.02 <0.02 <0.02	0.15 0.21 0.22 0.08	
La Fortesa, Spain/ 1993	1.00	1000	2/14	0 pulp 7 0 peel 7 7 whole (22.4 kg whole, 15.3 kg pulp, 7.1 kg peel)	<0.02 <0.02 0.22 0.05 0.02	<0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.16 0.14 0.05	2087/93 #0443-93
Neuville su Oise, France/ 1996	0.75	1000	1	0 pulp 2 0 whole 2 3 5	<0.02 <0.02 0.42 0.25 0.18 0.08	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.44 0.27 0.22 0.11	2155/96
Ecque-villy, France/ 1996	0.75	1000	1	3 pulp 0 whole 3	<0.02 0.19 0.18	<0.02 <0.02 <0.02	<0.02 0.21 0.23	2155/96
Crique-beuf sur Seine, France/ 1996	0.75	1000	1	3 pulp 5 0 whole 2 3 5	<0.02 <0.02 0.21 0.09 0.15 0.08	<0.02 <0.02 <0.02 <0.02 <0.02 <0.02	<0.02 <0.02 0.23 0.10 0.17 0.10	2155/96

In the trials in Portugal, method recoveries (0.02-0.5 mg/kg, n = 10) from fortified control pulp were 73-93% for methiocarb, 88-102% for methiocarb sulfone, and 98-119% for methiocarb sulfoxide. Recoveries at 0.02 and 0.1 mg/kg (n = 5) from pulp were 95-99% for methiocarb, 92-100% for methiocarb sulfone, and 100-111% for methiocarb sulfoxide in Spain, and 77-95% for methiocarb, 88-104% for methiocarb sulfone, and 81-132% for methiocarb sulfoxide in France.

Strawberries. Fourteen residue trials on strawberries were reported from Europe (Bayer AG, 1974a,b, 1975, 1989d, 1992d; Seym, 1993b, 1995b; Seym and Walz-Tylla, 1993c; Heinemann and Walz-Tylla, 1997). GAP in Southern and Northern Europe is as follows.

Country	Formulation	Rate, kg ai/ha	No. of applications	PHI, days
Southern Europe				
Italy	WP	1.2	1	21
Italy	RB	0.2	2	14
Portugal	WP	0.8	2	7
Spain	WP	1	2	15
Northern Europe				
Austria	RB	0.12	2	
Belgium	RB	0.20	2	
Germany	RB	0.12	2	14
Ireland	RB	0.22	1	
Sweden	RB	0.2	1	
UK	RB	0.22	1	7

The results of the trials are shown in Table 36. Samples were analysed by HPLC Method 00014, M004, except in those trials conducted in the 1970s, in which the residues were oxidized to methiocarb

sulfone and determined by GLC with an FPD, as in methods such as 00040/E003 (Drüger, 1982). The shorter GAP PHI of Portugal was applied to evaluate the trials in Spain. Samples were stored from 0.5-14 months before analysis.

Table 36. Residues of methiocarb and its metabolites in strawberries.

Location/year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	Form	kg ai/ha/ l/ha	No., days					
Palafolls, Spain/1990	50 WP	1.0/ 1000		0 4 7 10 14	1.1 0.50 0.23 0.12 <0.04	<0.04 <0.04 <0.04 <0.04 <0.04	0.05 0.19 0.13 0.13 0.07	0340-90
San Pol de Mar, Spain/1990	50 WP	1.0/ 1000	2/15	0 4 7 10 14	4.7 0.97 0.46 0.36 0.16	<0.04 <0.04 <0.04 <0.04 <0.04	0.26 0.38 0.37 0.21 0.12	021490
Callela, Spain/1991[1] (see processing)	50 WP	1.0/ 1000	2/12	7 10 14	0.35 0.12 0.09	<0.04 <0.04 <0.04	0.19 0.14 0.12	020191 0201-91
Angeles, Spain/1993[2] glasshouse	50 WP	0.9/903 1.0/1000 1.0/1000	3/14, 14	0 7 14	0.24 0.28 0.10	<0.02 <0.02 <0.02	0.10 0.15 0.10	2086/93 04493
Alenquer, Portugal/1993[2]	50 WP	1.1/1066 1.2/1200	2/14	0 9 14	0.46 0.18 0.06	<0.02 <0.02 <0.02	<0.02 0.27 0.23	2086/93 0447-93
Salvaterra de Magos, Portugal/1993[2] glasshouse	50 WP	1.0/ 1000	2/14	0 7 10 14	0.53 0.30 0.27 0.40	<0.02 <0.02 <0.02 <0.02	0.14 0.17 0.21 0.31	2086/93 0446-93
La Cellera de Ter, Spain/1996[3]	50 WP	0.92/740 1.0/800 1.0/800	3/14, 14	0 7 14 21	1.3 0.08 <0.02 <0.02	<0.02 <0.02 <0.02 <0.02	1.4 0.21 0.07 0.03	2154/96 0581-96
St. Cebria de Vallalta, Spain/1996[3]	50 WP	1.0/800	3/12, 14	0 7 14 21	0.38 0.04 <0.02 <0.02	<0.02 <.02 <0.02 <0.02	0.45 0.13 0.05 <0.02	2154/96 0767-96
Thurston, Suffolk, UK/1991[4]	4 RB	0.22	1	7 14	<0.02 <0.02	<0.02 <0.02	<0.02 <0.02	2139/91
Upchurch, Kent, UK/1991[4]	4 RB	0.22	1	7 14	<0.02 <0.02	<0.02 <0.02	<0.02 <0.02	2139/91
Bergen op Zoom, NL/ 1974	4 GR	0.12	1	3 7 14	<0.05 <0.05 <0.05			2103-74
Laacherhof, Germany/1974 (triplicate plots)	4 GR	0.12	1	3 7 10 14 21	<0.05 <0.05 <0.05 <0.05 <0.05			2100-74
Gorsem, Belgium/1975 (duplicate plots)	4 GR	0.16	1	0 4 7 14	<0.05 <0.05 <0.05 <0.05			2103-75

Location/year	Application			PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
	Form	kg ai/ha/ l/ha	No., days					
Nyborg, Denmark/1988 (triplicate plots)	4 GR	0.12	1	1 3 8 	0.10 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04 <0.04			0329-88; 0330-88; 0331-88

[1]Recoveries from fortified controls (0.04 mg/kg) were 86 and 88% for methiocarb, 88 and 110% for methiocarb sulfone, and 91 and 103% for methiocarb sulfoxide.
[2]Recoveries from fortified controls (0.02-0.2 mg/kg, n = 7) were 67-83% for methiocarb, 71-96% for methiocarb sulfone and 71-105% for methiocarb sulfoxide.
[3]Recoveries from fortified controls (0.02, 0.20 mg/kg, n = 4) were 69-89% for methiocarb, 94-105% for methiocarb sulfone and 88-100% for methiocarb sulfoxide.
[4]Recoveries from fortified controls (0.02-0.50 mg/kg, n = 8) were 71-84% for methiocarb, 65-95% for methiocarb sulfone and 86-107% for methiocarb sulfoxide.

Wheat. Numerous residue trials were reported for wheat, but the company requested the withdrawal of all except two reports of field trials with an RB formulation in the UK (Seym, 1993a). GAP for cereals in the UK specifies application of a 20 g/kg RB formulation at 0.15 kg ai/ha or a 40 g/kg RB formulation at 0.22 kg ai/ha, with a 7-day PHI. The number of applications is not specified. Admixture at seeding, spreading and aerial applications are permitted. In the two UK trials, one application was made at drilling together with the seed and the second was spread about the ground. Samples were analysed by HPLC Method 00014, E005. The results are shown in Table 37. Recoveries of methiocarb from forage (0.1 and 1.0 mg/kg) were 101, 94 and 95%, from grain (0.04 and 0.4 mg/kg) 100, 96 and 93%, and from straw 93, 94 and 75%. Recoveries of methiocarb sulfone from forage (0.1 and 1.0 mg/kg) were 123, 119 and 103%; from grain (0.04 and 0.4 mg/kg) 98, 97 and 97%, and from straw (0.1 and 1.0 mg/kg) 112, 114 and 79%. Recoveries for methiocarb sulfoxide from forage (0.1 and 1.0 mg/kg) were 72, 70 and 90%; from grain (0.04 and 0.4 mg/kg) 91, 90 and 98%, and from straw (0.1 and 1.0 mg/kg) 101, 99 and 90%. The samples were stored frozen for 20 months before analysis.

Table 37. Residues of methiocarb and its metabolites in wheat, UK, 1991 (Seym, 1993a).

Location	Appli-cation rate, kg ai/ha	No. of applications/ interval, days	PHI (days)	Sample	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
Thurston, Suffolk	0.22	2/48	0 94 94	Forage Grain Straw	≤0.1 ≤0.04 ≤0.1	≤0.1 ≤0.04 ≤0.1	≤0.1 ≤0.04 ≤0.1	2039/91
Pointon, Lincolnshire	0.22	2/62	0 98 98	Forage Grain Straw	≤0.1 ≤0.04 ≤0.1	≤0.1 ≤0.04 ≤0.1	≤0.2 ≤0.04 ≤0.1	2039/91

Barley. Field trials were reported from Germany (Bayer AG, 1980b). Additional trial data were withdrawn by Bayer. A 4% RB formulation was spread on the ground twice. Samples were analysed by GLC Method 00040 (171). The trial results are shown in Table 38. GAP for Germany is 2 applications at 0.1 kg ai/ha/application of a 4% RB formulation at drilling and/or up to growth stage 29. The PHI is 7 days. Samples were stored for 3-5 months before analysis.

Table 38. Residues of methiocarb and its metabolites in barley, Germany, 1980 (Bayer AG, 1980b).

Location/ year	Application rate, kg ai/ha	No. of applic./interval, days	PHI, days	Sample	Methiocarb + methiocarb sulfone + methiocarb sulfoxide), mg/kg	Report no.
Albig	0.12	2/14	0 14 92 92	Forage Forage Straw Grain	≤0.05 <0.05 ≤0.05 ≤0.05	2102-80
Bursheid	0.12	2/14	0 21 80 80	Forage Forage Straw Grain	≤0.05 <0.05 ≤0.05 ≤0.05	2101-80
Monheim	0.12	2/14	0 21 76 76	Forage Forage Straw Grain	≤0.05 <0.05 ≤0.05 ≤0.05	2100-80

Maize. Trials on maize after seed treatment or application during drilling were conducted in Germany with a 500 g/kg FS formulation (Bayer AG, 1982, 1983). No residues were detectable (<0.05 mg/kg each of methiocarb, methiocarb sulfone and methiocarb sulfoxide). GAP for Northern Europe (Austria, Belgium, Germany, The Netherlands) specifies a seed treatment at 0.5 kg ai per 100 kg seed. The results of the trials are shown in Table 39. Analyses were by GLC, Method 00040.

Table 39. Residues of methiocarb and its metabolites in maize, Germany (Bayer AG, 1982, 1983).

Location/year	Rate (kg ai/100 kg seed)	PHI, days	Sample	Residue, methiocarb + methiocarb sulfone + methiocarb sulfoxide, mg/kg	Report no.
Daubersbach, 1982	0.5 (0.15 kg ai/ha)	174	Kernel	≤0.05	2105-82
Rosenberg, 1982	0.5 (0.15 kg ai/ha)	178	Kernel	≤0.05	2104-82
Fadengreuth, 1982	0.5 (0.16 kg ai/ha)	169	Kernel	≤0.05	2103-82
Ascheberg, 1982	0.5 (0.12 kg ai/ha)	91 187	Forage Kernel	≤0.1 ≤0.05	2102-82
Klein-Niedesheim, 1982	0.5 (0.4 kg ai/ha; seed rate 80 kg/ha)	90	Forage	≤0.1	2101-82
Versuchsgut Laacherhof, 1982	0.5 (0.15 kg ai/ha; seed rate 30 kg/ha)	90 184	Forage Kernel	≤0.1 ≤0.05	2100-82
Rodingen, 1983	0.5 (0.15 kg ai/ha)	90 113	Forage Cob	≤0.1 ≤0.1	2103-83
Hartefeld, 1983	0.5 (0.15 kg ai/ha)	90 126	Forage Cob	≤0.1 ≤0.1	2102-83
Laacherhof, 1983	0.5 (0.15 kg ai/ha; seed rate 30 kg/ha)	90 156	Forage Cob	≤0.1 ≤0.1	2101-83
Höfchen, 1983	0.5 (0.15 kg ai/ha; seed rate 30 kg/ha)	90 152	Forage Cob	≤0.1 ≤0.1	2100-83

Hazelnuts. Five trials were reported from Turkey (Bayer AG, 1987). GAP for Turkey is one foliar application of a 500 g/kg WP formulation at 0.6 kg ai/ha, with a 90-day PHI. The samples (nut without shell) were analysed by HPLC Method 00014, with a stated limit of determination of 0.04 mg/kg per component. The results are shown in Table 40.

Table 40. Residues of methiocarb and its metabolites in hazelnuts (without the shell) (Bayer AG, 1987).

Location	Application rate, kg ai./ha	Vol., l/ha	PHI, days	Methio-carb, mg/kg	Methiocarb sulfone, mg/kg	Methiocarb sulfoxide, mg/kg	Report no.
Ordu-Unye-Inkur Akpinarkoye	0.75	200	90	≤0.04	≤0.04	≤0.04	2104-87
Giresun, Merkex-Usgurkoyu	0.75	100	86	≤0.04	≤0.04	≤0.04	2102-87
Giresun, Merkez-Citilak Kale mah	2 DP formulation 0.70	-	86	≤0.04	≤0.04	≤0.04	2103-87
Giresun, Kesap, Cakirli	2 DP formulation 0.70	-	87	≤0.04	≤0.04	≤0.04	2200-87
Giresun, Desap, Karaderekoyu	2 DP formulation 0.70	-	87	≤0.04	≤0.04	≤0.04	2101-87

Rape seed. Field trials were reported from Germany, with both a WP formulation (foliar application) and an RB formulation (ground application) (Bayer AG, 1979a,b, 1980a). GAP for Germany specifies two applications of a 20 g/kg RB formulation at 0.1 kg ai/ha with a 15-day PHI. No GAP was reported for the use of the WP formulation in Germany, but in France the WP formulation may be applied at 0.1 kg ai/hl, 15-day PHI, and in The Netherlands at 0.5 kg ai/ha in 200-600 l of water per hectare, one application only, PHI not specified. The results are shown in Table 41. Samples were analysed by GLC Method 171, with a stated limit of determination of 0.05 mg/kg. Samples were stored for 1-15 months before analysis.

Table 41. Residues of methiocarb and its metabolites in rape seed, Germany (Bayer AG, 1979a,b, 1980a).

Location/ year	Form.	Application rate, kg ai/ha/ vol., l/ha)	No. of applications/ interval, days	PHI, days	Sample	Residue, mg/kg (methiocarb + methiocarb sulfoxide + methiocarb sulfone)	Ref. No.
Gau-Odernheim/ 1979	50 WP	0.75/ 600	1	30 60 291 291	Forage Forage Straw Seed	≤0.05 <0.05 ≤0.05 ≤0.05	2100-79
Monheim/ 1979	50 WP	0.75/ 600	1	30 60 60 83 83	Forage Forage Pod Straw Seed	≤0.05 <0.05 <0.05 ≤0.05 ≤0.05	2100-79
Burscheid/ 1979	50 WP	0.75 600	1	129 59 59 96 96	Forage Forage Pod Straw Seed	<0.05 ≤0.05 <0.05 ≤0.05 ≤0.05	2100-79
Gau-Odernheim/ 1980	4 GR	0.12	2/14	0 14 61	Forage Forage Forage	<0.05 <0.05 <0.05	2106-80
Bursheid/ 1980	4 GR	0.12	2/14	0 21 98 98	Forage Forage Straw Seed	0.54 <0.05 <0.05 <0.05	2105-80
Monheim/ 1980	4 GR	0.12	2/14	0 21 108 108	Forage Forage Straw Seed Forage on day of first application	<0.05 <0.05 <0.05 <0.05 2.6	2104-80

Location/ year	Form.	Application rate, kg ai/ha/ vol., l/ha)	No. of applications/ interval, days	PHI, days	Sample	Residue, mg/kg (methiocarb + methiocarb sulfoxide + methiocarb sulfone)	Ref. No.
Pfalz/1980	4 GR	0.12	2/14	0 20 97	Forage Forage Seed	4.5 <0.05 <0.05	2113-80

Animal feeding studies

A poultry feeding study was conducted with methiocarb and methiocarb sulfoxide (9:1) (Strankowski and Minor, 1976; Chemagro, 1976). Twenty laying hens, approximately 25 weeks old, were acclimatized for a 2-week period, then divided into groups of four birds each and placed on a diet containing 0, 20, 60, 120 or 360 mg methiocarb/methiocarb sulfoxide per kg feed. Fresh ration (Purina) was supplied daily for 28 days with water *ad lib*. Food consumption was measured daily for each group. The calculated average intakes (mg methiocarb/methiocarb sulfoxide per kg bw per day) were 0, 1.3, 3.6, 6.3 and 24. Body weights and feed consumptions were not reported. Eggs were collected on even days, combined by group (without the shell) and stored frozen. Egg production was constant within each group over the trial period.

The hens were weighed before the study and immediately before slaughter. The 120 and 360 ppm groups showed a weight loss of 2-13%. Giblets, muscle, fat and skin were collected by group. Tissues and eggs were extracted and analysed for methiocarb and methiocarb sulfoxide. Details were not reported. The results of the analyses are shown in Table 42.

Table 42. Residues of methiocarb and methiocarb sulfoxide in poultry tissues and eggs (Strankowski and Minor, 1976).

Feed concentration, mg methiocarb + methiocarb sulfoxide per kg feed	Methiocarb + methiocarb sulfoxide, mg/kg				
	Giblets (heart, gizzard, liver)	Muscle	Skin	Fat	Eggs (28 days)
0	<0.02	<0.02	<0.02	<0.02	<0.02
20	<0.02				<0.02
60	0.06		<0.02		<0.02
120	0.13	<0.02	<0.02	<0.02	0.03
360	0.13	<0.02	0.02	<0.02	0.06

In a cattle feeding study (Chemagro, 1970a) two cows and seven beef cattle, in groups of three, were dosed with 0.30, 0.90, or 3.0 mg methiocarb/kg bw/day for 29 days, equivalent to 10, 30, or 100 ppm in the diet assuming that the livestock would consume 3% of total body weight in dry feed daily. Both cows were in the 100 ppm group. The animals were slaughtered after the last dose and tissues analysed for total methiocarb.

In a separate feeding study (Chemagro, 1970b) three groups of three dairy cows were fed diets containing 10, 30, or 100 ppm methiocarb for 29 days. Residues were reported in the milk from day 29 only.

The results of the two studies are shown in Table 43.

Table 43. Residues of methiocarb in milk and tissues from dairy cows and beef cattle (Chemagro, 1970a,b).

Feeding level (ppm)	Sample	Methiocarb, mg/kg
10	Liver	<0.05
	Kidney	<0.05
	Muscle	<0.05
	Omental fat	<0.05
	Renal fat	<0.05
	Back fat	<0.05
	Milk (day 29)	0.007
30	Liver	0.08
	Kidney	<0.05
	Muscle	<0.05
	Omental fat	<0.05
	Renal fat	<0.05
	Back fat	<0.05
	Milk (day 29)	0.020
100	Liver	0.10
	Kidney	0.08
	Muscle	<0.05
	Omental fat	<0.05
	Renal fat	<0.05
	Back fat	<0.05
	Milk (day 29)	0.033

The calculated dietary burden for poultry and cattle is shown in Table 44.

Table 44. Estimate of residue intake of methiocarb by farm animals.

	Feedstuff in diet, %	Dry matter in feedstuff, %	Residue in crop, mg/kg	Dietary burden, ppm in feed
Dairy cattle				
Maize				
grain	40	80	0.1 *	0.05
stover	10	83	0.1*	0.01
Cereal (wheat)				
forage	60	25	0.1*	0.24
Total	100			0.30
Beef Cattle				
Maize				
grain	60	80	0.1*	0.14
stover	0	83	0.1*	0.00
Cereal (wheat)				
forage	25	25	0.1*	0.120
Total	100			0.24
Poultry				
Maize				
grain	80	88	0.1*	0.09
Cereal (wheat)				
grain	20	89	0.05*	0.011
Total	80			0.1

The 0.1 ppm in the diet for poultry is less than one thousandth of the concentration at which residues were detected in poultry products in the feeding study. The 0.3 ppm in the diet for cattle is one thirtieth of the concentration at which no residues (<0.05 mg/kg) were found in tissues and at which the residue in milk was 0.007 mg/kg.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were provided.

In processing

Processing studies were reported on potatoes, peppers and strawberries.

Potatoes. Potatoes without a methiocarb residue (<0.02 mg/kg) from the UK field trials (Table 26) were thinly peeled, washed gently and cooked under pressure in water (12 min at 110˚C). The experiment was designed to mimic household preparation. As no residues (<0.02 mg/kg) were found in the peel or cooked potatoes processing factors could not be determined (Seym and Walz-Tylla, 1993a).

Strawberries. Strawberries from field trials in Callela, Spain (Table 36) were processed into jam and preserved fruit, using a household procedure (Seym and Walz-Tylla, 1993c). The strawberries contained 0.17 mg/kg methiocarb and 0.16 mg/kg methiocarb sulfoxide at the 7-day PHI. Damaged fruits and the calyx and stalks were removed. The strawberries were washed in standing water with slow movement, then minced and mixed with a jelly sugar. The mixture was stirred and brought to the boil for 10 minutes. The resulting jam was placed in polystyrene boxes. For preserved fruit, washed strawberries were mixed with a sugar solution and pasteurized in an autoclave. All samples were stored at –20°C until analysed by an HPLC procedure, 00014, M001, E007. The mass balance of the residues was not reported.

Recoveries from control samples of jam and preserve fortified at 0.04 mg/kg of each analyte were 63 and 65% in preserve and 83 and 90% in jam for methiocarb, 103 and 104% in preserve and 71 and 72% in jam for methiocarb sulfone, and 91 and 95% in preserve and 92 and 105% in jam for methiocarb sulfoxide.

The results are shown in Table 45.

Table 45. Effect on residues of processing strawberries containing methiocarb and methiocarb sulfoxide[1] (Seym and Walz-Tylla, 1993c).

Sample	Methiocarb		Methiocarb sulfoxide	
	mg/kg	processing factor	mg/kg	processing factor
Strawberry	0.35	-	0.19	-
Washed strawberry	0.17	0.48	0.16	0.84
Strawberry jam	0.08	0.23	0.12	0.63
Strawberry preserve	0.09	0.26	0.09	0.47

[1]Methiocarb sulfone was absent from the fruit and processed fractions (<0.04 mg/kg).

Peppers. Processing studies (Seym, 1997; Seym and Walz-Tylla, 1993b) were conducted on peppers from field trials in Spain and Portugal (Table 32). The peppers from Spain (two trials) were washed and canned, and those from Portugal were washed. The results are shown in Table 46.

Table 46. Effect on residues of methiocarb and its sulfoxide[1] in peppers of washing and canning (Seym, 1997; Seym and Walz-Tylla, 1993b).

Location	Sample	PHI, days	Methiocarb		Methiocarb sulfoxide	
			mg/kg	processing factor	mg/kg	processing factor
Malgrat, Spain	Fruit	7	0.82	-	0.38	-
	Fruit washed	7	0.20	0.24	0.20	0.53
	Preserved	7	0.07	0.08	0.07	0.18
	Fruit	10	0.28	-	0.22	-
	Fruit washed	10	0.25	0.89	0.23	1.0
	Preserved	10	0.04	0.14	<0.04	0.18
Viladecans, Spain	Fruit	7	1.1	-	0.43	-
	Fruit washed	7	0.26	0.24	0.29	0.67
	Preserved	7	0.13	0.12	0.07	0.16
	Fruit	10	0.15	0.14	0.14	0.32
	Fruit washed	10	0.14	0.13	0.10	0.23
	Preserved	10	<0.04	0.04	<0.04	0.09
Bordinheira, Portugal	Fruit	7	0.13	-	0.10	-
	Fruit washed	7	0.06	0.46	0.09	0.90
	Fruit	14	0.03	0.23	0.03	0.30
	Fruit washed	14	<0.02	0.15	<0.02	0.20

[1]Methiocarb sulfone was absent from all samples.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Information was supplied by the governments of Australia and The Netherlands. Results of the analysis of fruit and vegetable samples purchased weekly from the Sydney wholesale markets are shown in Table 47.

Table 47. Monitoring of methiocarb residues in Australia (Sydney) from 1989 to 1995.

Commodity	No. of samples	No. with residues >0.01 mg/kg
Grapes	94	5 (< MRL of 0.1 mg/kg)
Strawberries	113	1 (< MRL of 0.1 mg/kg)
Citrus	1	0
Apples	1	0
Pears	2	0
Cherries	48	0
Nectarines	28	0
Peaches	139	0
Onion	1	0
Broccoli	2	0
Zucchini	1	0
Lettuce	1	0
Capsicum (pepper)	1	0
Mushroom	1	0
Tomato	1	0
Beans	2	0
Carrot	1	0
Potato	1	0
Celery	102	0

The Netherlands submitted monitoring data on residues of methiocarb in food in commerce for the period 1994-1996 and for 1997. The results are shown in Tables 48 and 49.

Table 48. Residues of methiocarb in food in commerce in The Netherlands, 1995-1996.

Commodity	No. of samples analysed	No. with residues ≥0.05 mg/kg (LOD)	Residues, mg/kg
Pome fruit	1496	0	
Apple			
Stone fruit	437	0	
Plums			
Berries and small fruit	667	1	0.24
Grapes, strawberries			
Miscellaneous fruit	191	1	0.07
Mangoes			
Root and tuber vegetables	1010	0	
Radish			
Bulb vegetables	97	0	
Onions			
Fruiting vegetables	1108	0	
Tomato	1525	4	0.05-0.34
Pepper (sweet)	951	0	
Cucumbers	206	0	
Courgettes			
Brassica vegetables	297	3	0.05-1.0
Chinese cabbage			
Leafy vegetables and fresh herbs			
Lamb's lettuce	268	0	
Lettuce	3306	0	
Iceberg lettuce	471	0	
Endive	1137	0	
Parsley	368	2	0.05
Stem vegetables	233	0	
Celery			
Other arable products	699	1	0.09
Processed products	23	0	

Table 49. Residues of methiocarb in food in commerce in The Netherlands, 1997.

Commodity	No. of samples analysed	No. with residues ≥0.05 mg/kg (LOD)	Residues, mg/kg
Berries and small fruits			
Grapes	196	1	0.22
Strawberries	779	4	0.05-1.3
Other fruits and fruit products	152	1	0.10
Root and tuber vegetables	164	1	1.4
Carrots			
Fruiting vegetables			
Peppers (sweet)	607	12	0.05-1.6
Cucumbers	249		
Brassica vegetables	116	1	1.1
Chinese cabbage			
Leaf vegetables and fresh herbs			
Lambs lettuce			
Lettuce	53		
Endive	828	1	1.1
Chervil	366	1	1.5
Parsley	8	1	0.09
Other leafy vegetables	85	1	0.08
	114	4	0.12-1.6
Stem vegetables	187	2	0.05-0.34
Celery			

NATIONAL MAXIMUM RESIDUE LIMITS

National MRLs were reported by Bayer AG and by the governments of Australia and The Netherlands.

Country, Residue definition Commodity	MRL, mg/kg	Notes
Argentina		
Sum of methiocarb, its sulfoxide and sulfone, expressed as methiocarb		
Apple	0.01	
Garlic	0.05	
Lettuce	0.2	
Onion	0.05	
Peach	0.1	
Pear	0.01	
Tomato	0.02 T	
Citrus fruit	0.1	
Grape	0.5	
Grape wine	0.1	
Other fruit	0.1 T	
Vegetables	0.1	
Wine	0.1	
Austria		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Fruit	0.2	
Lettuce	1	
Other plant commodities	0.05	
Belgium		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Cabbage	0.1	
Cucumber	0.3	
Leafy vegetables	1	
Leek	0.1	
Other plant commodities	0	<LOD 0.05 mg/kg
Croatia		
Hazel nut	0.05	
Maize/Corn	0.05	
Other vegetables	0.1	
Rape	0.05	
Root vegetables	0.2	
Sunflower	0.05	
Finland		
Plum	0.5	
France		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Berries	0.1	
Lettuce	0.2	
Other vegetables	0.1	
Rape	0.1	
Germany		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Lettuce and similar	1	
Other plant commodities	0.1	
Pome fruit	0.2	
Israel		
Sum of methiocarb, its sulfoxide and sulfone, expressed as methiocarb		
Forage crops	0.01	
Fruit	0.01	
Vegetables	0.01	
Italy		
Alfalfa	0.05	

Country, Residue definition Commodity	MRL, mg/kg	Notes
Almond	0.05	
Artichoke	0.05	
Asparagus	0.05	
Aubergine	0.05	
Bean	0.05	
Bean green	0.05	
Beet, sugar	0.05	
Cabbage	0.05	
Carrot	0.05	
Celery	0.05	
Clover	0.05	
Cucurbits	0.05	
Fennel, common	0.05	
Grape	0.05	
Herbs	0.05	
Leafy vegetables	0.05	
Lettuce and similar	0.05	
Other solanacea	0.05	
Pea, garden without pods	0.05	
Pepper, sweet	0.05	
Pome fruit	0.05	
Potato	0.05	
Radish	0.05	
Spinach and similar	0.05	
Stone fruit	0.05	
Strawberry	0.05	
Tobacco	0.05	
Tomato	0.05	
Luxembourg		
Lettuce	1	
Other plant commodities	0.05	
Pome fruit	0.2	
Malaysia		
Fruit	0.05	
Leafy vegetables	0.1	
Rice	0.5	
Root vegetables	0.1	
Vegetables excluding leafy vegetables	0.1	
Netherlands		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb sulfone		
Cucumber	0.5	
Flowering brassicas	0.1	
Head brassicas	0.1	
Leafy vegetables	1	
Lettuce and similar	1	
Melon	0.5	
Other vegetables	0.05	At or about the LOD
Leeks	1	
New Zealand		
Blueberry	25	
Cherry	7	
Paraguay		
Rice grain, hulled	0.05	
South Africa		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Apple	0.2	
Apple	0.05 E	
Apricot	0.05 E	
Citrus fruit	0.1	

Country, Residue definition Commodity	MRL, mg/kg	Notes
Grape	0.2	
Grape	0.05 E	
Nectarine	0.05 E	
Peach	0.05 E	
Pear	0.2	
Pear	0.05 E	
Plum	0.2	
Plum	0.05 E	
South Korea		
Barley	0.05	
Buckwheat, common	0.05	
Cabbage	0.2	
Cherry	5	
Grapefruit	0.05	
Lemon	0.05	
Oat	0.05	
Orange	0.05	
Other cereals	0.05	
Other citrus fruit	0.05	
Pe-tsai	0.2	
Peach	5	
Rice	0.05	
Rye	0.05	
Sorghum grain	0.05	
Wheat	0.05	
Spain		
Sum of methiocarb, its sulfoxide and its sulfone, expressed as methiocarb		
Bean pods and/or immature seeds	0.2	
Beet, sugar	0.05	
Berry, wild	0.05	
Brassica vegetables	0.05	
Bulb vegetables	0.05	
Cacao	0.05	
Cereals	0.05	
Citrus fruit	0.05	
Coffee	0.05	
Cola	0.05	
Corn, sweet	0.05	
Cucumber	0.2	
Forage crops and straw	0.05	
Fruit and vegetables, dried	0.05	
Grape	0.05	
Herbs	0.05	
Hop	0.05	
Leafy vegetables	0.05	
Mushroom	0.05	
Nuts	0.05	
Oil plants seed	0.05	
Other berries and small fruits	0.05	
Other cucurbits with edible peel	0.05	
Other cucurbits with inedible peel	0.05	
Other legume vegetables	0.05	
Other solanacea	0.05	
Pea pods and/or immature seeds	0.2	
Pepper, sweet	1	
Pome fruit	0.05	
Potato	0.05	
Pulses	0.05	
Root and tuber vegetables	0.05	

Country, Residue definition Commodity	MRL, mg/kg	Notes
Rubus-Species (Cane fruit)	0.05	
Spices	0.05	
Stem vegetables	0.05	
Stone fruit	0.05	
Strawberry	0.2	
Sugar cane	0.05	
Tea	0.05	
Tobacco	0.05	
Tomato	0.2	
Tropical and subtropical fruit	0.05	
Switzerland		
Sum of methiocarb, its sulfoxide and sulfone, expressed as methiocarb		
All plant commodities	0.05	<LOD
Taiwan		
Sum of methiocarb, its sulfoxide and sulfone		
Melon	0.5	
Melon, Water-	0.5	
Uruguay		
Rice grain, hulled	0.05	
USA		
Methiocarb and cholinesterase-inhibiting metabolites		
Citrus fruit	0.02	
Corn, sweet (corn-on-the-cob)	0.03	
Maize/Corn fodder	0.03	
Maize/Corn forage	0.03	
Maize/Corn fresh	0.03	
Maize/Corn grain	0.03	
Peach	5	
Popcorn grain	0.03	

T = Temporary tolerance
E = Export tolerance
LOD = Limit of determination

APPRAISAL

Methiocarb was identified by the 1995 CCPR as a candidate for periodic review (ALINORM 95/24A, Annex 1). The periodic review of toxicology was in 1998 and the present evaluation is a periodic review of residue aspects. The most recent extensive residue reviews were in 1981 and 1983.

Animal metabolism

The metabolism of [*phenyl*-1-^{14}C]methiocarb was studied in rats, dairy cows and chickens.

[*Phenyl*-1-^{14}C]methiocarb was administered at dose levels of 20 and 0.25 mg/kg body weight to rats. Most of the administered radioactivity was excreted with the urine in 48 hours, >90% in the high-dose group and >70% in the low-dose group. The main metabolites in the organic extracts of the urine were methiocarb phenol and methiocarb sulfoxide phenol. The same study was evaluated in the 1998 review of the toxicology.

A dairy cow (500 kg) was dosed by capsule with radiolabelled methiocarb at 0.14 mg/kg bw/day for 5 consecutive days. The residue in the milk peaked at 0.062 mg/kg as methiocarb on day 3. The total residues in the meat and fat were not quantifiable, <0.01 mg/kg. The total residues in the kidneys and liver were 0.108 and 0.073 mg/kg respectively. The following metabolites were identified, by TLC only, in milk: methiocarb sulfoxide phenol and conjugates 27% of the TRR; methiocarb sulfone phenol and

conjugates 26% of the TRR; methiocarb sulfoxide 3% of the TRR; in kidney: methiocarb phenol and conjugate 55% of the TRR; methiocarb sulfoxide phenol 7% of the TRR; methiocarb sulfone phenol 17% of the TRR; in liver: methiocarb phenol and conjugate 25% of the TRR; methiocarb sulfoxide phenol and conjugate, 9% of the TRR; methiocarb sulfone phenol and conjugate 6% of the TRR; methiocarb and conjugate 14% of the TRR. Methiocarb was found only in the liver.

Eight hens were dosed with [^{14}C]methiocarb for 5 consecutive days at 4.4 mg/kg bw/day. All eggs contained <0.1 mg/kg methiocarb equivalents. The total residues were 0.45 mg/kg in the muscle, 0.7 mg/kg in fat, 2.0 mg/kg in liver and 3.3 mg/kg in kidney.

Tissue extracts were analysed by two-dimensional TLC only. The main residues in fat were methiocarb 41% of the TRR, methiocarb phenol and conjugate 26%, methiocarb sulfoxide phenol and conjugate 9% and *N*-hydroxymethyl-methiocarb 7% of the TRR. The main radioactive compounds in the muscle were methiocarb 7% of the TRR, methiocarb phenol and conjugate 16%, methiocarb sulfoxide phenol and conjugate 28% and *N*-hydroxymethyl-methiocarb sulfoxide 17%. The main residue in the liver were methiocarb phenol and conjugate 17% of the TRR, methiocarb sulfoxide phenol and conjugate 24%, methiocarb sulfone phenol and conjugate 11% and *N*-hydroxymethyl-methiocarb sulfoxide 6% of the TRR.

The Meeting concluded that the livestock metabolism studies were marginally acceptable and that the metabolism of methiocarb in ruminants and poultry was sufficiently understood. Critical data, such as feed consumption to determine the concentration of the administered pesticide on a feed basis, were not provided. Identifications were based only on TLC and should have been confirmed by other techniques. No detailed information was supplied on the periods of storage of the samples and extracts before analysis or of the stability of methiocarb and its metabolites under the storage conditions.

Methiocarb is extensively metabolized in ruminants and poultry by ester cleavage, followed by oxidation of the resulting phenol to the sulfoxide and sulfone. A competing pathway observed only in hens is hydroxylation of the carbamate methyl and oxidation of the sulfur to sulfoxide. The metabolites found in rat urine suggest a similar metabolism.

Plant metabolism

Studies were on rice, tomatoes, lettuce and apples.

In the apple study, [*phenyl*-1-^{14}C]methiocarb was applied directly to the surface of apples on a tree with a syringe, with both single and multiple applications. The total residue on the apples after the last of 8 treatments was 4.52 mg/kg as methiocarb, of which 0.67 mg/kg was in the pulp. Of the total radioactive residue, 24% was in the benzene wash of the whole apple, 60% in the peel and 15% in the pulp. The residue in the whole apple consisted of 61% methiocarb, 6.5% methiocarb sulfoxide, 4.6% methiocarb phenol, 22% methiocarb sulfoxide phenol and 1.1% methiocarb sulfone phenol.

In a study of the translocation of [*phenyl*-1-^{14}C]methiocarb from soil to lettuce and tomato seedlings the methiocarb was applied at 1.12 kg ai/ha to the sandy soil in which the plants were growing. Translocation was rapid. Seven days after the application, 45% of the applied radioactivity was in the lettuce plants and 26% was in the tomato plants.

Rice at the soft dough stage was sprayed with [*phenyl*-1-^{14}C]methiocarb at 2.24 kg ai/ha. Some plants were sprayed again at the same rate 9 days later. The plants were harvested 0, 6, 14, 21 or 28 days after the first or second application and separated into grain heads and stalks. In both rice grain and stalks, 95–98% of the recovered radioactivity was organosoluble on the day of application, but this decreased to 63–72% 28 days after both single and double applications. The organic extracts of grain and stalks were analysed only by TLC. The composition of the residue in the organic extracts on the day of the single application was 94% methiocarb, 2% methiocarb sulfoxide and about 1% each of methiocarb sulfone

phenol and methiocarb sulfoxide phenol in the stalks. *N*-hydroxymethyl-methiocarb sulfoxide was also detected in later samples. After 28 days the organic extract contained 11% methiocarb, 32% methiocarb sulfoxide, 11% methiocarb sulfoxide phenol and 3% each of *N*-hydroxymethyl-methiocarb sulfoxide and methiocarb sulfone in the grain and 20% methiocarb, 36% methiocarb sulfoxide, 10% methiocarb sulfoxide phenol and 2% methiocarb sulfone phenol in the stalks.

The Meeting concluded that the plant metabolism studies were marginally satisfactory and adequately defined the metabolism of methiocarb in plants. Only the studies on apples and rice determined the nature of the residues in the edible portions and the overall ^{14}C balance could not be determined from the information provided. Identifications were by TLC only: other techniques should have been used to confirm identities and to investigate unidentified compounds. No information was provided on the periods of storage of the samples and extracts or the stability of methiocarb and its metabolites under the storage conditions. The studies are not representative of such major uses as seed treatment and application to the soil as a bait or by incorporation.

Methiocarb is readily translocated. Metabolism is by ester cleavage and oxidation of the resulting phenols to sulfoxides and sulfones. The parent compound may also undergo conversion to the sulfoxide and sulfone and *N*-hydroxymethyl compounds. The metabolic products in livestock and plants are similar.

Environmental fate

Rotational crops. Two studies were conducted. In the first, radiolabelled methiocarb was incorporated into sandy loam soil at 5.6 kg ai/ha. Sweet corn was planted as the main crop and harvested at normal maturity. The land lay fallow until the following year when rotational crops of wheat, sugar beet and spinach were planted. At 399 days after application wheat forage contained 0.15 mg/kg methiocarb equivalents and sugar beet tops contained 0.108 mg/kg. At 450 days after application, sugar beet tops contained 0.071 mg/kg methiocarb equivalents, roots contained 0.252 mg/kg and spinach contained 0.225 mg/kg. Spinach taken 450 days after application and wheat heads (0.066 mg/kg), stalks (0.141 mg/kg) and forage (0.323 mg/kg) from 551 days after application were extracted and the extracts analysed by TLC. The main residue component in spinach was methiocarb sulfoxide phenol, 26% of the total radioactive residue (0.058 mg/kg). The main compounds in wheat forage were methiocarb sulfoxide at 12% (0.039 mg/kg) and methiocarb sulfone at 10%, in wheat stalks methiocarb sulfoxide phenol at 7% and methiocarb sulfone at 8% (0.011 mg/kg) and in the wheat heads *N*-hydroxymethyl-methiocarb 12% (0.008 mg/kg), methiocarb sulfoxide phenol at 14% and methiocarb sulfone at 11%.

In the second study, unlabelled methiocarb was applied to bare soils in the USA at rates of 1.4–11.2 kg ai/ha. Rotational crops (sorghum, wheat, snap beans, peas, carrots, radishes, maize, corn, black-eyed-peas, turnips) were planted at intervals of 30 days during 365 days after the application. Samples were analysed for combined residues of methiocarb, methiocarb sulfone and methiocarb sulfoxide. No residues were detected (<0.02 mg/kg total) in any edible portion of the vegetables or grain planted 30 or more days after application of the methiocarb at rates up to 11.2 kg ai/ha. Green vines and green forage contained total residues after treatment at 11.2 kg ai/ha of 0.14 mg/kg in corn forage (30-day plantback), 0.15 and 0.07 mg/kg in black-eyed pea vines at 30 and 90-day plantbacks respectively and 0.29 mg/kg in turnip tops (30-day plantback).

Degradation in soil

Soil was treated with 7 mg/kg [*phenyl*-1-^{14}C]methiocarb, equivalent to 11.5 kg ai/ha and watered weekly. Samples were taken at intervals up to 16 weeks, extracted and analysed by TLC. The proportion of organic- and water-extractable radioactivity decreased from 76% at week 4 to 67% at week 16. The distribution of radioactivity changed slightly during the period. Methiocarb accounted for 49% of the applied radioactivity at 4 weeks and 30% at 16 weeks. Methiocarb sulfoxide and its conjugate remained constant at 20–22% of the applied radioactivity. Methiocarb sulfoxide phenol increased from 5.3% to 15%.

A more detailed study under aerobic conditions with dry sandy loam soil at an application rate of 1.44 mg/kg showed that extractable residues decreased from 100% of the applied radioactivity on day 0 to 27% on day 217 and bound residues increased to 43% over the same period. Radioactive carbon dioxide appeared on day 29 and increased to 30% of the applied radioactivity on day 217. Methiocarb decreased from 96% of the residue on day 0 to 3% on day 217. On day 29 the main radioactive compounds as a percentage of the applied radioactivity were methiocarb 24%, methiocarb sulfoxide 30%, methiocarb sulfoxide phenol 16%, methiocarb sulfone 1% and methiocarb sulfone phenol 3%. The degradation followed biphasic first-order kinetics, with half lives of 17.7 days and 111 days.

A soil sample from the above experiment was taken after 14 days and the conditions made anaerobic by covering the sample with water (pH 5) and purging continuously with nitrogen. The system was sampled 0–64 days after conversion to the anaerobic environment. The extractable proportion decreased only slightly, from 87 to 76%. Methiocarb decreased from 55% to 27% and methiocarb phenol increased from 0 to 47%. Methiocarb sulfoxide was readily hydrolysed to methiocarb sulfoxide phenol. Volatile compounds accounted for <4% of applied radioactivity.

A more recent study with radiolabelled methiocarb applied to soil at a rate of 100 g ai/ha was not made available to the Meeting, but new half-lives based on first order kinetics were calculated in various types of soil. Under aerobic conditions, methiocarb had a half-life of 1–2 days and methiocarb sulfoxide a half-life of 2–6 days.

The photolysis of [*phenyl*-1-^{14}C]methiocarb on the surface of sandy loam soil exposed to natural sunlight was compared with controls maintained in the dark. After 30 days methiocarb accounted for 47% of the radiolabelled residue on irradiated soil and 75% on control soil. The main product was methiocarb sulfoxide, 23% of the radiolabelled residue on irradiated soil at 30 days and 3.1% on the control soil. Both photolytic and non-photolytic degradation was occurring. Calculated half-lives were 28 days for irradiated samples and 81 days for dark controls.

Adsorption and desorption constants for various soils were determined for [*phenyl*-1-^{14}C]methiocarb, [*phenyl*-1-^{14}C]methiocarb phenol, [1-*phenyl*-^{14}C]methiocarb sulfoxide and [*phenyl*-1-^{14}C]methiocarb sulfoxide phenol. Methiocarb sulfoxide was rapidly degraded and was not adsorbed by soil; within 24 hours of application the soil contained only methiocarb sulfoxide phenol. Methiocarb showed moderately high K_d values, suggesting significant adsorption to all types of soil. The K_d for adsorption ranged from 4.3 ml/g in sandy loam to 9.0 ml/g in silt loam and for desorption from 6.7 in sandy loam to 16.2 in silt loam. The K_d for adsorption of methiocarb sulfoxide phenol ranged from 0.19 in sand to 0.66 in sandy loam and for desorption from 0.74 in sand to 1.6 in silty clay. Methiocarb sulfoxide phenol showed low adsorption to all the soils.

In a leaching experiment [*phenyl*-1-^{14}C]methiocarb was added to sandy loam soil at 37 mg/kg. The soil was aged aerobically for 30 days and an aliquot was extracted and analysed. The residues in the aged soil consisted of 80% methiocarb, 7% methiocarb sulfoxide, 6% methiocarb sulfoxide phenol and 6% insoluble. The leaching rate with 0.01 N aqueous calcium chloride solution through sand, sandy loam and silty loam was compared. Over a 5-day period 1.1 l of the aqueous solution was passed through columns of soil topped with the treated soil (20 g). The leachate from sand, sandy loam and silty loam contained 23%, 7% and 3% of the applied radioactivity respectively. Sand retained 71% of the applied radioactivity, sandy loam 92% and silty loam 93%. The sand leachate contained 2% methiocarb and 12% methiocarb sulfoxide and the sandy loam and silty loam contained more methiocarb sulfoxide than methiocarb, although the concentrations were very low. The results indicate that methiocarb sulfoxide is more readily leached than methiocarb.

Fate in water/sediment systems. The degradation of [*phenyl*-1-^{14}C]methiocarb in aerobic and anaerobic aquatic systems was investigated. The radiolabelled material was added to pond water at 2 mg/l in glass jars. For the anaerobic study, preconditioned soil was also added. The jars were wrapped in black plastic

and maintained in a greenhouse. Jars were removed at intervals of 0–112 days and the contents radio-analysed, extracted and the extracts analysed by TLC. In the aerobic system methiocarb disappeared in 3 days and in the anaerobic system 5% remained after 7 days. By day 56 42% of the radioactivity was bound to the soil in the anaerobic system. The main products in the aerobic system (water phase) were methiocarb phenol and methiocarb sulfoxide phenol. The main product in the anaerobic system was methiocarb phenol.

The half-lives of [*phenyl*-1-^{14}C]methiocarb in buffered aqueous solutions were determined in the dark at 25°C. On the basis of first-order kinetics, the half-lives were 320, 21 and 0.21 days at pH 5, 7 and 9 respectively. Methiocarb is unstable under alkaline conditions. At pH 5 the main product was methiocarb sulfoxide (1-9%) and at pH 7 methiocarb phenol, 46% at day 30. At pH 9 after 7 days, the main compounds were methiocarb phenol 78% and methiocarb sulfoxide phenol 10%. At pH 5 and 7 about 1% of *N*-hydroxymethyl-methiocarb was found and at pH 9 about 1% of *N*-hydroxymethyl-methiocarb sulfone.

The photochemical degradation of [*phenyl*-1-^{14}C]methiocarb in pH 5.0 aqueous solution at 25°C exposed in quartz tubes to natural sunlight for 30 days. Controls were maintained in the dark. The only product identified was methiocarb sulfoxide, 13% of the applied radioactivity when irradiated and 1% in the dark. The photolysis half-life was calculated as 88 days and 128 days corrected for non-photolytic degradation.

The Meeting concluded that the environmental fate of methiocarb is adequately known. In both soil and aqueous environments, methiocarb is degraded to the sulfoxide or loses the carbamate group, yielding methiocarb phenol. The half-life of methiocarb in soil has been variously determined as 1–2 days and 18 days, with the former more reflective of typical concentrations of methiocarb in soil. Methiocarb is relatively stable to sunlight, both on soil and in water. It is adsorbed by soils of various types and is not readily leached, whereas methiocarb sulfoxide is leached. Methiocarb sulfoxide phenol is formed by the rapid degradation of methiocarb sulfoxide in soil and is not adsorbed by a range of soils. Methiocarb is unstable in alkaline aqueous solutions with a half-life of 0.21 days.

The degradation products found in soil and water do not differ from those found in plant metabolism studies, except methiocarb sulfone quinone, which accounted for 8% of the extractable radioactivity in sandy loam soil incubated under aerobic conditions in the dark for 217 days.

Analytical methods

Numerous analytical methods are available both for data collection and for enforcement. Generally, the GLC methods determine the sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone as methiocarb sulfone after a potassium permanganate oxidation step. The HPLC methods determine methiocarb, methiocarb sulfone and methiocarb sulfoxide as individual compounds.

In the GLC methods, such as Bayer Method 171 and DFG Method 79-A-1, plant samples are extracted with acetone and 0.5 N HCl. The filtrate is extracted with chloroform and the chloroform solvent changed to acetone. The acetone solution is precipitated with ammonium chloride and phosphoric acid, the filtrate extracted with chloroform and the chloroform again changed to acetone. This solution is oxidized with 0.1 M potassium permanganate for 15 minutes at room temperature. The residues are silylated and determined by GLC with a flame photometric detector. Variations of the sample preparation are available for milk and animal tissues. Calibration is with external standards, using a log-log calibration curve. The validated limit of determination is 0.05 mg/kg except for milk, for which it is 0.005 mg/kg.

In Bayer Method 172 basic hydrolysis follows the permanganate oxidation. The resulting sulfones and sulfone phenols are cleaned up, derivatized and determined as before. The limit of determination is 0.01 mg/kg. Recoveries are generally >80%.

Method I340 is a modification of Bayer Method 172 for poultry commodities. The ground tissue sample is extracted with acetonitrile and partitioned with hexane. Eggs are blended with acetone and partitioned with methylene chloride. The solvent is changed to acetonitrile and the solution is partitioned with hexane. The acetonitrile extracts of tissues and eggs are evaporated, redissolved in acetone and precipitated with ammonium chloride solution. The mixture is filtered and oxidized as in Method 171. The methylene chloride extract of the oxidation mixture is hydrolysed with sodium hydroxide, 2.5 N at 60°C for 30 min. The hydrolysis products are derivatized with BSTFA and determined as in Method 171. A capillary column is specified. The limit of determination is 0.02 mg/kg.

HPLC methods, such as Bayer Method 00014 and its many modifications, employ specific extraction procedures for green foliage of grain, fatty substrates (nuts) and fat-free materials (cucumber). Modification M004 is specifically designed for strawberries, melons, tomatoes, leek, lettuce and bell peppers. Plant material is macerated with methylene chloride and the extract is concentrated to an aqueous residue, to which is added salt, HCl (for strawberries, leeks and melons only) and water. The solution is cleaned up on a solid-phase extraction column and the methylene chloride eluate is analysed by HPLC.

HPLC includes post-column hydrolysis (0.05 N caustic soda, 90°C) and derivatization with *o*-phthalaldehyde and mercaptoethanol in borate buffer. The methylamine released by the basic hydrolysis of the carbamate reacts with the derivatizing agent to form 1-hydroxyethylthio)-2-methylisoindole, detected by fluorescence. Fortified recoveries indicate limits of determination of 0.04 or 0.02 mg/kg for each analyte, with limits of detection of about 0.006 mg/kg.

The Meeting concluded that adequate analytical methods exist for enforcement and data collection for methiocarb, methiocarb sulfoxide and methiocarb sulfone.

Stability of residues in stored analytical samples

Methiocarb and methiocarb sulfoxide were stable in blueberries stored frozen for 118 days at–23^{o}C. The study was performed with samples fortified at 2.8 mg/kg and 3.3 mg/kg with radiolabelled methiocarb and methiocarb sulfoxide respectively. The percentage remaining was approximately 99% after the storage interval.

Summary information only was supplied on the stability (at 0 to –10^{o}C) of methiocarb, methiocarb sulfoxide and methiocarb sulfone in beans, grapes, cabbage, rice, tomatoes, broccoli, Brussels sprouts and cauliflower. Except for Brussels sprouts and broccoli, the data indicated that methiocarb and the metabolites are stable for up to 380 days. Details were not provided and concurrent method recoveries were not performed at each storage interval.

Samples from field trials were stored frozen for 1 month to 2 years before analysis.

The Meeting concluded that the information on storage stability is inadequate, except for berries, and that the residues reported from field trials might be understated if methiocarb and its sulfone and sulfoxide metabolites are unstable under the storage conditions used for the samples. Understated residues will give rise to the estimation of erroneous maximum residue levels and STMRs. The Meeting therefore concluded that the validity of the trials (except on berries) could not be assured and recommended the withdrawal of all existing MRLs. The Meeting could not recommend MRLs except for strawberries, pending the review of adequate data on storage stability. Maximum residue levels were provisionally estimated however.

Definition of the residue

Plant and animal metabolism studies indicate that methiocarb is extensively metabolized to phenolic derivatives by cleavage of the carbamate and by oxidation of methiocarb and the phenolic derivatives to

sulfoxides and sulfones. A minor metabolic path involves hydroxylation of the carbamate methyl group and oxidation to the corresponding sulfoxide. The analytical methods determine methiocarb, methiocarb sulfoxide and methiocarb sulfone, either as methiocarb sulfone or individually. The current definition of the residue is "sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb".

The 1998 toxicology review established both a chronic ADI and an acute reference dose for methiocarb. It was noted that methiocarb sulfoxide, as well as methiocarb, is of acute dietary concern.

The Meeting concluded that the residue should be defined both for enforcement of MRLs and for the estimations of dietary intake as "the sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb".

Residues resulting from supervised trials

Residues reported as below the LOD (limit of determination) for the individual components of the residue were assigned the value of the LOD. For example if methiocarb, methiocarb sulfoxide and methiocarb sulfone were each <0.02 mg/kg on cabbage, the value used for deriving the MRL and the STMR would be 0.02 mg/kg. If the method determined the three compounds as one derivative and the result was reported as below the LOD, the value of the LOD was again used, for example <0.05 mg/kg total residue would be taken as 0.05 mg/kg. For residues with individual component(s) exceeding the LOD, the residue was taken as being the sum of the residues exceeding the LOD. For example if the residue on cabbage was reported as 0.15 mg/kg methiocarb, <0.02 mg/kg methiocarb sulfoxide and 0.06 mg/kg methiocarb sulfone, the residue would be taken to be 0.21 mg/kg. This procedure is appropriate, as the residue in many cases is predominantly (60%) one compound.

Potatoes. Two trials were reported from the UK. GAP is 3 ground applications of an RB formulation at 0.22 kg ai/ha with no specified PHI. The UK trials complied with GAP with PHIs of 18 and 20 days. The residues were not quantifiable (<0.02 mg/kg).

The Meeting could not estimate a maximum residue level or STMR because two trials were an inadequate number.

Leeks. Eleven field trials were reported from France and The Netherlands. GAP for France was not reported. In The Netherlands, up to 2 foliar applications of an SC formulation, 500 g/l, may be made at rates of 0.5-0.75 kg ai/ha, with a 14-day PHI. GAP is similar for Belgium, but the PHI is 21 days. The trials in France were evaluated against Belgian GAP. One trial in The Netherlands did not comply with GAP, because the PHI was 21 days.

The residues in rank order were 0.02, 0.03, 0.08, 0.14, 0.18, 0.25, 0.29 (2), 0.30 and 0.39 mg/kg. The Meeting estimated a provisional STMR of 0.22 mg/kg and a maximum residue level of 0.5 mg/kg.

Cabbages. Fifteen field trials were reported from Austria, Belgium, Germany and The Netherlands. GAP for Austria specifies 2 foliar applications of a WP formulation at 0.5 kg ai/ha with a 14-day PHI or a spreading application of an RB formulation at 0.12 kg ai/ha with a 14-day PHI. GAP for Belgium allows 3 foliar applications of an SC formulation at 0.75 kg ai/ha with a 14-day PHI or 2 spreading applications of an RB formulation at 0.12 kg ai/ha with a 14-day PHI. In Germany GAP requires 2 applications of an RB formulation at 0.12 kg ai/ha with a 14-day PHI and in The Netherlands one foliar application of a WP formulation at 1.5 kg ai/ha with a 14-day PHI.

Six trials in Germany complied with maximum GAP for the RB formulation and eight in Germany, Belgium and The Netherlands with Belgian GAP for the SC formulation.

The residues in rank order were 0.02 (4), 0.03 (4) and 0.05 (6) mg/kg. The Meeting estimated a provisional STMR of 0.03 mg/kg and a maximum residue level of 0.1 mg/kg.

Cauliflowers. Four trials were reported from Germany, where GAP is two baiting applications of an RB or GB formulation at 0.12 kg ai/ha with a 14-day PHI. Four trials were conducted under maximum GAP conditions, but the incorrect commodity was analysed in one trial. The three relevant residues were all <0.05 mg/kg.

The Meeting agreed that four trials were inadequate for the estimation of a maximum residue level and STMR, but concluded that the data on cabbages could be extrapolated to cauliflowers since GAP is identical and the application is ground, not foliar where differences in plant habit might lead to different residue levels. The Meeting estimated a provisional maximum residue level and STMR for cauliflower of 0.1 mg/kg and 0.03 mg/kg respectively.

Artichokes. Two trials were reported from Italy. The only reported GAP is for Israel: one foliar application of a WP formulation at 1.75 kg ai/ha, no PHI specified. The Italian trials did not comply with this GAP.

No maximum residue level or STMR could be estimated.

Peas. Eight trials were reported from Germany. GAP is a seed treatment at 0.5 l of a 500 g/l FS formulation per 100 kg of seed. The eight trials were under maximum GAP conditions and quantifiable residues were found in only one trial.

The residues in the peas were 0.05 (7) and 0.08 mg/kg. The residues in the pea vines were 0.05 (7) and 0.04 mg/kg. The Meeting estimated a provisional STMR for peas and vines of 0.05 mg/kg each and maximum residue levels of 0.1 mg/kg and 0.05 mg/kg respectively.

Pepper. Five trials were reported from Spain and 2 glasshouse trials from Portugal. GAP for Spain is 3 foliar applications of a WP formulation, each 1.0 kg ai/ha, with a 7-day PHI. GAP for Portugal is the same, but with a 14-day PHI. The more demanding PHI of Spain was applied to the trials in Portugal. Six trials were at maximum GAP and one was at an application rate more than 30% above the maximum.

The residues in the six trials in rank order were 0.27, 0.49, 0.84, 0.92, 1.33 and 1.53 mg/kg. The Meeting estimated an STMR of 0.88 mg/kg and a maximum residue level of 2 mg/kg.

Tomatoes. Eight trials were reported: 1 from Portugal and 7 from Spain. GAP for both Spain and Portugal specifies 2 foliar applications of a WP formulation at 1.0 kg ai/ha, with a 7-day PHI, for both field and glasshouse applications. Two glasshouse trials in Spain were at more than 30% above GAP rate, with residues at 7 days of 0.22 and 0.59 mg/kg. The remaining six trials were under maximum GAP conditions.

The residues in rank order were 0.04 (2), 0.11, 0.17 (2) and 0.81 mg/kg, the last from a glasshouse trial. The Meeting estimated a provisional STMR of 0.14 mg/kg and a maximum residue level of 1 mg/kg.

Cucumbers. Six trials were reported: 4 from France and 2 from Spain. The French trials were in glasshouses. GAP for France was not reported. GAP for Spain, against which the trials in France were evaluated, is 2 foliar applications of a WP formulation at 1.0 kg ai/ha, with a 7-day PHI. The six trials were at or within 30% of maximum GAP.

The residues in rank order were 0.04 (2), 0.07, 0.09, 0.11 and 0.12 mg/kg. The Meeting estimated a provisional STMR of 0.08 mg/kg and a maximum residue level of 0.2 mg/kg.

Melons. Seven trials were reported: 3 from France, 2 glasshouse from Portugal and 2 from Spain. No GAP was reported for France and Spain, but the trials can be covered by GAP in Portugal and Italy (two foliar applications of a WP formulation at 1.0 kg ai/ha, with a 7-day PHI). Six trials were at or within 30% of maximum GAP, but the analyses in Spain and Portugal were of the pulp and peel, not whole melons. The residue in the whole melons was calculated from the reported weights of peel and pulp. In 1 trial in France the PHI was more than 30% below GAP.

The residues in the whole melons in rank order were 0.07, 0.17, 0.18, 0.19, 0.26 and 0.49 mg/kg and in the pulp 0.02 (4) and 0.06 (2) mg/kg. The Meeting estimated a provisional STMR of 0.02 mg/kg and a maximum residue level of 1 mg/kg.

Strawberries. Fourteen trials were reported: 6 from Spain, 2 from Portugal, 1 from Germany, 1 from Denmark, 1 from Belgium, 1 from The Netherlands and 2 from the UK. GAP in Portugal and Spain calls for 2 foliar applications of a WP formulation at 0.8 and 1.0 kg ai/ha respectively, with 7- and 15-day PHIs respectively. The shorter PHI of Portugal was applied to evaluate the trials in Spain. GAP in northern Europe requires the ground application of an RB formulation: in Belgium 2 applications, each 0.20 kg ai/ha, no PHI; in Germany 2 applications, each 0.12 kg ai/ha, 14-day PHI; in the UK 1 application, 0.22 kg ai/ha, 7-day PHI and in Sweden 1 application, 0.2 kg ai/ha, no PHI. GAP in Denmark and The Netherlands was not reported. German GAP was applied to evaluate the trials in The Netherlands and Denmark. All trials were at or within 30% of maximum GAP.

The residues from the application of a granular formulation to the ground in rank order were 0.02 (2), 0.04 and 0.05 (3) mg/kg; and from foliar applications of a WP formulation 0.17, 0.29, 0.36, 0.43, 0.45, 0.54, 0.71 and 0.83 mg/kg. The latter is the critical GAP. The Meeting estimated an STMR of 0.44 mg/kg and a maximum residue level of 1 mg/kg.

Cereal grains. Two trials on wheat were reported from the UK, where GAP for cereal grains requires application of an RB formulation at 0.15 kg ai/ha–0.20 kg ai/ha, with a 7-day PHI. The number of applications is not specified. In the field trials two applications were made, one at drilling and one on the ground 94 and 98 days before harvest of grain and straw and 0 days before the harvest of forage. Three barley trials were reported from Germany. GAP for barley, oats, rye, wheat and triticale specifies up to 2 applications of an RB formulation at 0.1 kg ai/ha. The PHI is not specified, although the practical PHI is governed by the growth stage, up to growth stage 29. The trials were at or within 30% of maximum GAP. No quantifiable residues were found in the grain, straw and fodder of wheat or barley. The residues in the grain, straw and fodder in rank order were <0.04 (2), <0.05 (3) mg/kg, <0.05 (3), <0.1 (2) mg/kg, <0.05 (3) and <0.1 (2) mg/kg respectively.

The Meeting concluded that the use of a bait formulation applied to the surface of the ground and not incorporated into the soil is unlikely to leave methiocarb residues in the grain commodities. The Meeting therefore judged five trials to be adequate for this GAP and estimated provisional maximum residue levels of 0.05*, 0.1* and 0.1* mg/kg for the grain, straw and fodder respectively of barley, oats, rye, wheat and triticale. The Meeting also estimated STMRs of 0 mg/kg for the grain, straw and fodder of these cereals.

Ten trials on maize in Germany were according to GAP: seed treatment or application at drilling with an FS formulation at 0.5 kg ai/100 kg seed.

The residues in maize grain (kernel and cob) in rank order were <0.05 (5) and <0.1 (4) mg/kg. The residues in the forage were all <0.1 mg/kg (6 samples).

The Meeting estimated provisional STMRs of 0 mg/kg and maximum residue levels of 0.1* mg/kg for maize grain and forage.

Rape seed. Seven trials were reported from Germany, where GAP specifies two applications of an RB formulation at 0.1 kg ai/ha with no specified PHI. The practical PHI is at growth stage 29–30. Three trials were with foliar application of a WP formulation for which no GAP in Germany was reported, but the trials were evaluated against GAP in The Netherlands (one foliar application of the WP formulation at 0.5 kg ai/ha with no specified PHI). These three trials were within 30% of the maximum GAP conditions. The remaining four trials were with a GR formulation, not RB. Residues from the granular formulation were found in rape forage on the day of application in two of the four trials at 0.54 and 2.6 mg/kg.

The Meeting regarded three trials with a foliar application as too few for the estimation of a maximum residue level or an STMR and recommended withdrawal of the existing MRL.

Hazelnuts. Five trials were conducted in Turkey where GAP is one foliar application of a WP formulation at 0.6 kg ai/ha, with a 90-day PHI. Nuts without shells were analysed. All the trials were at maximum GAP and all 5 residues were below the LOD of 0.05 mg/kg.

The Meeting estimated a provisional STMR of 0.05 mg/kg and a maximum residue level of 0.05* mg/kg.

No residue trials were reported for artichokes, broccoli, Brussels sprouts, citrus, lettuce, sugar beet or sweet corn. The Meeting recommended the withdrawal of the existing MRLs.

Animal feeding studies

In a poultry feeding study hens were fed a diet containing methiocarb and methiocarb sulfoxide (9:1) for 28 days, at rates ranging from 0 to 360 ppm in the feed. At 120 ppm residues were below the limit of determination (<0.02 mg/kg) in muscle, skin and fat, 0.03 mg/kg in eggs and 0.13 mg/kg in giblets (liver, etc.). At 360 ppm residues were <0.02 mg/kg in the muscle and fat, 0.02 mg/kg in skin, 0.06 mg/kg in eggs and 0.13 mg/kg in giblets.

A dairy cow feeding study was reported in which the animals were dosed daily for 29 days with the equivalent of 0, 10, 30 and 100 ppm methiocarb in the feed. Maximum total methiocarb residues in milk on day 29 were 0.007 mg/kg at the 10 ppm feeding level, 0.020 mg/kg at the 30 ppm level and 0.033 mg/kg at the 100 ppm level. No residues (<0.05 mg/kg total methiocarb) were found in any tissue at any feeding level, except 0.08-0.1 mg/kg total methiocarb in liver at 30 and in kidney at 100 ppm.

The livestock feed items for which provisional maximum residue levels were estimated were maize grain, maize forage (ruminant feed only), pea vines (ruminant only), cereal grains and cereal forages (ruminant only). The residues in all these except pea vines were below the limits of determination. From the estimated maximum residue levels, 0.1* mg/kg for maize grain and forage, 0.05* mg/kg for cereal grains, 0.1* mg/kg for cereal forages and 0.05 mg/kg for pea vines, the diets were calculated to contain methiocarb residues of 0.1 ppm for poultry, 0.24 ppm for beef cattle and 0.30 ppm for dairy cattle.

The 0.1 ppm diet for poultry is at least a factor of 1000 below the concentration at which residues were detected in poultry products in the feeding study. The Meeting concluded that poultry maximum residue levels could be estimated at the practical limit of determination of the analytical methods, 0.05* mg/kg, and STMRs at 0 mg/kg for poultry meat and eggs.

The estimated low concentrations of methiocarb and metabolites in the ruminant diet, about 0.3 ppm, might be expected to yield residues below the enforcement limits of determination (0.005 mg/kg for milk, 0.05 mg/kg for tissues). Assuming a 600 kg animal and a dietary intake of 20 kg/day, the intake can be estimated at 0.000010 g methiocarb/kg bw/day. This is an order of magnitude below the dosing level in the metabolism study (0.00014 g/kg bw/day). In that study, the total fat and muscle residues were each <0.01 mg/kg and the total milk residue was 0.06 mg/kg. In the ruminant feeding study, no residues (<0.05

mg/kg) were found in any commodity after 29 days at a 10 ppm feeding level (30 times the maximum theoretical intake), except in milk at 0.007 mg/kg. The metabolism and feeding studies both indicate that total methiocarb residues in ruminant commodities will be below the limits of determination of the analytical methods (<0.02–0.05 mg/kg, 0.005 mg/kg for milk). The Meeting estimated provisional maximum residue levels for ruminant commodities at the practical limit of determination, 0.05* mg/kg for tissues and 0.01 mg/kg for milk, and STMRs for milk and ruminant tissues at 0 mg/kg.

Fate of residues in storage and processing

No relevant studies were reported. Processing studies for the preparation of strawberry jam and preserves and for the canning of peppers were reported to the Meeting. A potato processing study was reported, but the residue on the potatoes was below the limit of determination.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting recommended withdrawal of the existing CXLs but recommended an MRL and estimated an STMR for strawberry as shown below.

Definition of the residue for compliance with MRLs and estimation of dietary intake: sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb.

CCN	Commodity	MRLs , mg/kg		STMR
		New	Previous	mg/kg
VS 0620	Artichoke, Globe	W	0.05 *	
VB0400	Broccoli	W	0.2	
VB0402	Brussels sprouts	W	0.2	
VB0041	Cabbages, Head	W	0.2	
VB0404	Cauliflower	W	0.2	
GC0080	Cereal grains	W	0.05 *	
FC 0001	Citrus fruits	W	0.05 *	
PE 0112	Eggs	W	0.05 *	
TN 0666	Hazelnuts	W	0.05 *	
VL 0482	Lettuce, Head	W	0.2	
VL 0483	Lettuce, Leaf	W	0.2	
MM0095	Meat (from mammals other than marine mammals)	W	0.05 *	
ML0106	Milks	W	0.05 *	
PM 0110	Poultry meat	W	0.05 *	
SO 0495	Rape seed	W	0.05 *	
FB 0275	Strawberry	1		0.44
VR 0596	Sugar beet	W	0.05 *	
VO 0447	Sweet corn (corn-on-the-cob)	W	0.05 *	

FURTHER WORK OR INFORMATION

Desirable

1. A study of the stability of residues in stored analytical samples covering the crops and storage conditions of the trials reported in support of MRLs. The residue trials data reviewed above may be used after adequate storage stability has been demonstrated.

2. Metabolism studies, plant and livestock, including a demonstration of the stability of methiocarb and its metabolites in the samples and extracts.

DIETARY RISK ASSESSMENT

Chronic intake

The Meeting recommended withdrawal of the existing CXLs, but recommended an MRL and estimated an STMR for strawberry. The International Estimated Daily Intakes (IEDIs) for the 5 GEMS/Food regional diets, based on the single STMR, were 0% of the ADI. The Meeting concluded that the intake of residues of methiocarb resulting from the one use that has been considered by the JMPR is unlikely to present a public health concern. The Meeting agreed that a new assessment of chronic dietary risk should be carried out if new MRLs are recommended.

Acute intake

The International Estimate of Short Term Intake (IESTI) was 23% of the acute RfD for the general population and 38% for children for strawberries, the one food commodity considered. The Meeting concluded that the intake of residues of methiocarb resulting from the use that has been considered by the JMPR is unlikely to present a public health concern.

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Bayer AG. 1992c. Residue trials with Mesurol 50WP in tomato in Spain. Unpublished report no.: 0212-90.

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OXYDEMETON-METHYL (166)

EXPLANATION

The 1992 JMPR carried out a complete re-evaluation of oxydemeton-methyl, and this compound and demeton-S-methyl were also the subject of a periodic review by the 1998 JMPR. At the 31st Session of the CCPR (ALINORM 99/24A, para. 98), the JMPR was asked to clarify whether demeton-S-methyl and demeton-S-methylsulphon should remain in the residue definition of oxydemeton-methyl since it was believed that registrations of these compounds would not be retained in the future.

APPRAISAL

Both demeton-S-methyl and oxydemeton-methyl are used as insecticides. Extensive information was provided for the periodic review of oxydemeton-methyl but the only information reported for demeton-S-methyl was on its metabolism in wheat. Residues were defined as the sum of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon, expressed as oxydemeton-methyl, both for compliance with MRLs and for the estimation of dietary intake.

Oxydemeton-methyl is the sulfoxide of demeton-S-methyl. It is metabolised similarly in plants and mammalian systems to form demeton-S-methylsulphon, which is commonly known as oxydemeton-methyl sulfone or ODM sulfone. In studies with radiolabelled compounds ODM sulfone formed a major part of the identified radioactivity in goat kidneys, muscle and fat, and wheat straw and grain, and was a minor metabolite in cabbages and rats. ODM sulfone is considered to be significantly more toxic than demeton-S-methyl or oxydemeton-methyl.

Numerous methods of analysis were reviewed. These were similar and all determined the combined residue of demeton-S-methyl, oxydemeton-methyl and demeton-S-methylsulphon after an oxidation step that converted demeton-S-methyl and oxydemeton-methyl to the sulfone. All supervised trials were with formulations containing oxydemeton-methyl, analyses were by methods which oxidized the residues to ODM sulfone, and all residues were expressed as the sum of oxydemeton-methyl and ODM sulfone.

The Meeting concluded that if demeton-S-methyl were no longer supported, its residues should no longer contribute to the total demeton-S-methylsulphon. However, its exclusion from the defined residue could lead to difficulties in enforcement situations where the misuse of demeton-S-methyl might have occurred.

The Meeting therefore recommended that additional information should be sought from the CCPR. Member governments should be asked to comment on their national situations relating to current enforcement methods and possible difficulties which might arise as a result of amending the residue definition. Also, the registrants and national governments should be asked to comment on the registration status of demeton-S-methyl.

2-PHENYLPHENOL AND ITS SODIUM SALT (056)

EXPLANATION

2-Phenylphenol (ortho-phenylphenol, OPP), and sodium *o*-phenylphenate, SOPP, were first evaluated by the 1962 JECFA for their use for the post-harvest treatment of fruits and vegetables to protect against microbial damage during storage and distribution in commerce. A second evaluation by the 1964 JECFA provided specifications of the identity and purity of OPP and SOPP, and established an ADI. The 1969 JMPR recommended MRLs for 2-phenylphenol and its sodium salt in several fruits.

2-Phenylphenol was originally scheduled for periodic re-evaluation of residue aspects at the 1994 JMPR. The 1994 CCPR withdrew the compound from the agenda because the manufacturer (Bayer AG) indicated that it was not supporting the existing CXLs, and that the database was considered insufficient to support a periodic review. GAP was available only for citrus fruits and pears. Meanwhile the CCPR requested countries to submit additional data to support the MRLs, in the absence of which they would be deleted. The US delegation to the CCPR requested retention of the CXLs for citrus fruits and pears pending the development of additional information, and the delegate from Spain indicated an interest in an MRL for apples, so only these three CXLs were retained (ALINORM 95/24, para. 143-145). The California Citrus Quality Council (CCQC) and the Oregon Washington California Pear Bureau (now the Pear Bureau Northwest) undertook to support the extensive studies necessary for the re-registration of SOPP by the US EPA for the post-harvest treatment of fresh citrus fruit and pears grown in the USA.

At the 1995 CCPR the periodic re-evaluation of the residue data was scheduled for the 1999 JMPR (ALINORM 95/24A, Appendix IV). In 1997 the CCQC requested the WHO Joint Secretary to schedule a toxicological evaluation of additional studies with OPP/SOPP in experimental animals. The 1998 CCPR scheduled this evaluation for the 1999 JMPR, together with the periodic review of residue aspects. The 1998 CCPR noted that the CXL for apple would be considered for deletion at its next Session if not supported (ALINORM 99/24, para. 47).

The CCQC and the Pear Bureau Northwest provided, through Leng Associates of Midland, Michigan, USA, the information in support of the periodic review of 2-phenylphenol. Additional information was supplied by the governments of The Netherlands and Australia.

IDENTITIES

ISO common names:

2-phenylphenol (accepted in lieu of a common name)
2-phenylphenol-sodium

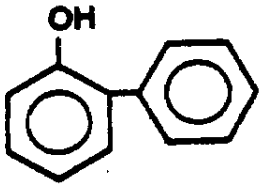
Chemical names:

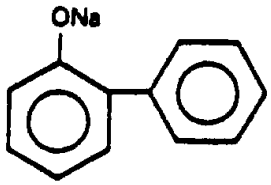
IUPAC:	biphenyl-2-ol	IUPAC:	sodium biphenyl-2-olate
CA:	(1,1'-biphenyl)-2-ol	CA:	biphenyl-2-ol, sodium salt
CAS No:	90-43-7	CAS No:	132-27-4 (and 6152-33-6)

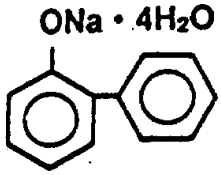
Synonyms:

ortho-biphenylol, *ortho*-phenylphenol, OPP	sodium 2-phenylphenate, SOPP, SOPP•$4H_2O$
ortho-hydroxybiphenyl, 2-hydroxybiphenyl	sodium *o*-phenylphenate, NaOPP

Structural formulae:







Molecular formula: $C_{12}H_{10}O$

Molecular weight: 170.2

Molecular formula: $C_{12}H_9NaO$ (and $\bullet 4H_2O$)

Molecular weight: 192.2 (and 264.3)

Physical and chemical properties

Pure active ingredient (OPP)

Vapour pressure: 1.6×10^{-3} mm Hg (2.16×10^{-4} kPa) at 25ºC

Melting point: 57ºC

Octanol/water partition coefficient:
log P_{OW}: 3.12 (20^{o} C,pH 7)

Solubility, g/kg solvent (20ºC):
0.76 in water (pH 5.67)
496 in methanol
479 in acetone
532 in acetonitrile
529 in octanol
466 in toluene
48.6 in hexane

Density: 1.2 g/ml at 25ºC

Hydrolysis: stable (25^{o}C, pH 5, 7, 9)

Photolysis: stable (10 days)

Technical OPP (Dowicide 1)

Purity: >99%

Appearance: white to light buff crystals

Commercial products

"Dowicide 1" Antimicrobial, >99% OPP, The Dow Chemical Co., Midland MI USA

SOPP anhydrous

1.8×10^{-9} mmHg (2.4×10^{-10} kPa) at 25^{o}C

m.p.: 298ºC (loss of H_2O at 120ºC)

Dissociation constant (tetrahydrate):
pKa: 9.84 at 20ºC

Solubility (tetrahydrate): g/kg solvent (20ºC)
534 in water (pH 13.61)
526 in methanol
543 in acetone
531 in acetonitrile
439 in octanol
0.53 in toluene
0.047 in hexane

Dissociates in water

Photolysis: stable (10 days)

Technical SOPP tetrahydrate (Dowicide A)

Purity: >97% tetrahydrate

Appearance:white crystalline flakes

"Dowicide A" Antimicrobial, >97% SOPP as tetrahydrate, The Dow Chemical Co., USA

"Preventol O Extra", Bayer Corp., USA, and Bayer AG, Leverkusen, Germany

"Preventol ON Extra", Bayer Corp., USA, and Bayer AG, Leverkusen, Germany

Formulations

Many formulated products containing OPP are registered in the USA and are approved world-wide for use as disinfectants, antimicrobials, preservatives, antioxidants, and sanitizing solutions in various industries.

Several formulated products containing SOPP are registered in the USA for the post-harvest treatment of fruits and vegetables to control microbial and fungal infections during storage and distribution.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Two lactating Nubian goats, 2 to 4 years of age, were given single daily oral encapsulated doses of [^{14}C]2-phenylphenol, labelled in the hydroxylated ring (99.5% chemical and radiochemical purity), for 5 consecutive days at an average level of 13.7 or 53.3 mg/day (Thalacker, 1997). The doses were equivalent to 11.3 ppm (174,500 dpm/µg) and 32.1 ppm (179,300 dpm/µg) of the test material in the diet, based on the actual feed consumption during the test period. A third goat was given placebos. Milk, urine, and faeces were collected daily from each animal. The goats were slaughtered about 23 hours after the last dose, and samples of blood, kidneys, liver, muscle (round), fat (omental and renal, mixed), urine, and gastrointestinal tract were collected and stored at –20^{o}C.

^{14}C was measured in all the samples. The urine from days 1-5 contained 80-83% of the total administered radioactivity. The faeces contained 4.3% of the low dose and 10% of the high dose. The cage washes contained 7% of the radioactivity from the low dose and 1.3% from the high dose. More than 90% of the administered radioactivity was eliminated from both goats.

The radioactivity in the milk of both animals reached a plateau on day 1 or 2 equivalent to 0.03% of the dose, 0.008 µg/g as phenylphenol for the low-dose goat and 0.043 µg/g for the high-dose goat.

The concentrations of radioactivity in the tissues are shown in Table 1.

Table 1. Radioactivity in tissues after oral administration of [^{14}C]phenylphenol to lactating goats for 5 consecutive days.

Sample	^{14}C, µg/g as phenylphenol	
	11.3 ppm rate	32.1 ppm rate
Fat	<0.0005	0.003
Kidneys	0.005	0.020
Liver	0.004	0.014
Muscle	<0.001	<0.001

Milk samples from each of the five days were extracted with acetone. The acetone was evaporated and the residual aqueous fraction partitioned with hexane. The radioactivity of each fraction was measured. The aqueous fraction contained 87% of the total radioactivity in the milk from the low-dose goat and 76% of that from the high-dose goat. The unextractable ^{14}C was 5% for the low-dose and 9% for the high-dose goat. Liver and kidney samples were extracted sequentially with acetonitrile and methanol/water (80:20). The residual solids were dried and assayed for radioactivity. About 83% of the total radioactive residue in the kidneys of the low-dose goat partitioned into acetonitrile and 13% into the methanol/water fraction. The proportions were 94% and 8% respectively

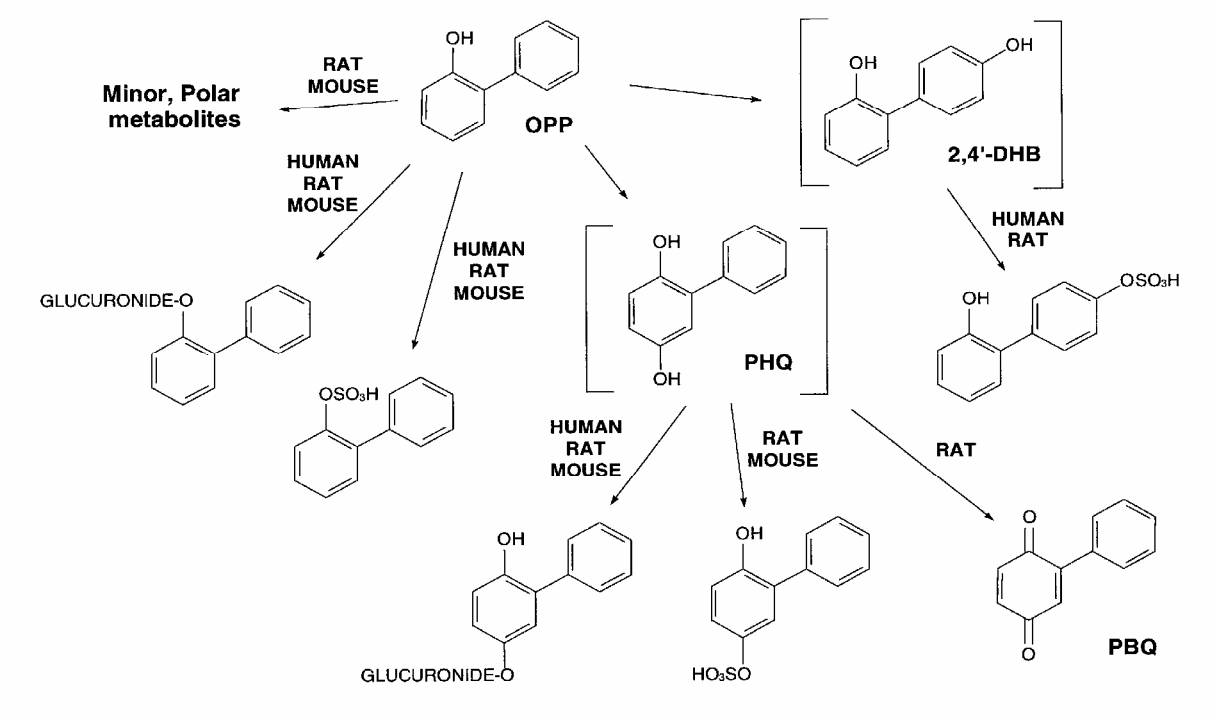
for the high-dose goat. In the liver samples 28% of the total radioactive residue partitioned into acetonitrile from the low-dose and 37% from the high-dose goat. About 20% partitioned into methanol/water from each goat. Unextractable ^{14}C amounted to 56% from the low dose and 45% from the high dose.

The extracts of milk, kidney and liver were analysed by HPLC, except the hexane extracts of milk because the levels of radioactivity were so low. Reference standards included phenyl-1,4-benzoquinone (PBQ), 2-phenylphenol and phenylhydroquinone (PHQ). Most of the attempted identification was by comparison with standards on a MicroBondapak C-18 column with a water/methanol (1.5% formic acid) gradient. No peak corresponded to any of the reference standards in any extract. The highest single residue detected was 0.007 mg/kg as OPP in the acetonitrile extract of kidneys. No other component accounted for more than 0.002 mg/kg.

The high dose rate, equivalent to 32 ppm in the feed, represents approximately six times the theoretical intake of OPP by cattle. This is based on the highest residue found in citrus trials according to GAP, 6.5 mg/kg, the average processing factor for converting oranges to dried pulp, 3.6, and the proportion of citrus pulp in the diet, 20%. At this six-fold rate more than 90% of the residue was eliminated. There was no propensity for the residue to accumulate in fat or muscle. Low levels were found in the milk (0.04 mg/kg), kidneys (0.02 mg/kg) and liver (0.01 mg/kg). The residues in these samples consisted of multiple components, none of which exceeded 0.007 mg/kg. Neither OPP nor PHQ were found. Measurable residues would therefore not be expected to result from the intake of OPP derived from uses according to GAP, assuming that additional bioaccumulation does not occur during exposure for more than 5 days.

The metabolism of 2-phenylphenol in rats, mice and humans was reviewed by Leng (1998). Studies conducted by the Dow Chemical Company and Bayer Corporation indicated the metabolic pathways shown in Figure 1. Metabolism studies have shown that OPP is absorbed well and excreted rapidly in the urine. The major metabolite excreted by rats is OPP sulfate with lesser amounts of the glucuronide conjugates of OPP and its hydroxylated metabolite, 2,5-biphenyldiol (phenylhyroquinone or PHQ). Trace amounts of phenyl-1,4-benzoquinone (PBQ) were also detected in the urine. Formation of the sulfate appeared to become saturated at a dose of about 600 mg/kg bw/day while the other conjugates increased in proportion to the dose up to the highest dose of about 1000 mg/kg bw/day. These metabolites were also found in the urine of mice given 5 daily doses of OPP at 25 or 1000 mg/kg bw and in human male volunteers given a dermal dose of [^{14}C]OPP at 0.006 mg/kg bw. The sulfate conjugate of 2,4'-biphenyldiol (2,4'-dihydroxybiphenyl, DHB) was also identified. Little or no free OPP, and no free PHQ or PBQ, were found in mice, rats or humans.

Figure 1. Metabolism of 2-phenylphenol (OPP) in rats, mice and man deduced from the analysis of urine.



A poultry metabolism study was not submitted, but current GAP does not include use on any poultry feed items.

Plant metabolism

Studies on oranges and pears were reported. Navel oranges (106, weighing from 145 to 191 g each) were dipped in a 0.1% solution and gently agitated for 3 minutes. The solution, maintained at 37˚C, consisted of a mixture of ring-^{14}C-labelled and unlabelled SOPP (Deccosol 122 concentrate) in distilled water adjusted to pH 11.8. The specific activity of the dosing solution was 8667 dpm/µg. This solution left a total residue of about 10 mg/kg on the oranges. Eight more oranges were dipped in a 0.5% solution. The oranges were air-dried on a stainless steel rack for about 2 hours and then packed into an incubator maintained at 90% relative humidity and 11.7˚C. After four weeks the incubator temperature was lowered to 5˚C to retard fruit spoilage.

Samples of eight oranges were collected after 2 hours, 2 days and 1, 2, 4, 6, 8, 10 and 12 weeks. Each orange was rinsed with methanol to remove surface residues, then peeled and cut into eight slices. The peeled oranges were processed through a juicer to yield juice and pulp, and the peels were chopped and homogenized in liquid nitrogen. The total radioactive residue was determined in each of the three substrates.

Homogenized peel (25 g) was extracted sequentially with hexane and methanol. The residual solid from the 12-week peel only was then sequentially incubated with cellulase (pH 5 buffer, 24 hours, 37˚C), refluxed with 1 N HCl (110˚C, 4 hours) and refluxed with 25% NaOH (110˚C, 26 hours). At each step the aqueous filtrate was extracted with ethyl acetate. The juice from the 12-week sampling only and the pulp from the high-dose treatment (0.5% dip) were also extracted with ethyl acetate. All the extracts and residual solids were radioanalysed.

The methanol rinse and hexane and methanol extracts from the peel at every sampling interval, the ethyl acetate extract from the high-dose pulp and the ethyl acetate extract from the 12-week juice were analysed by reversed-phase HPLC on a Nucleosil 5 C-18 100 A column, with a UV detector (254 nm) and a flow-through radioactivity monitor. Fractions were also collected and analysed by LSC. TLC was also used for separation and purification with normal-phase silica plates, which were scanned with a radioanalytical imaging system. Reference standards were 4,4'-biphenyldiol, phenylhydroquinone (PHQ), 2,2'-biphenyldiol, phenyl-1,4-benzoquinone, OPP, 2-methoxybiphenyl (2-MBP) and dibenzofuran.

Various peaks isolated by HPLC, particularly from rinse samples, were analysed by GC-MS with a double-focusing magnetic sector spectrometer operated in the electron impact mode, connected to an Rt_x 1 column, 30 m x 0.25 mm i.d..

The change in distribution of the radioactive residue with time is shown in Table 2. The residue migrated from the surface of the oranges into the peel, but there was very little further translocation. Less than 0.5% of the TRR was found in the juice or pulp at any time.

Table 2. Distribution of radioactivity in oranges at intervals after a 0.1% dip treatment with radiolabelled OPP.

Time	TRR, mg/kg[1]	Rinse, % of TRR	Juice, % of TRR	Pulp, % of TRR	Peel, % of TRR
2 h	9.8	58	0.17	0.16	42
2 days	12	24	0.21	0.13	76
7 days	10	12	0.30	0.16	94
2 weeks	10	6.0	0.33	0.23	94
4 weeks	8.4	5.8	0.32	0.21	94
6 weeks	8.4	3.9	0.34	0.28	95
8 weeks	9.8	5.8	0.34	0.36	94
10 weeks	9.8	4.7	0.31	0.28	95
12 weeks	9.2	4.8	0.23	0.18	95
12 weeks– 0.5% dip	16	5.3	0.44	0.39	94

[1]From ^{14}C in all fractions of all 8 oranges at each sampling

The distribution of the radioactivity in the peel among the hexane, methanol and residual solid fractions changed with time. The hexane-soluble portion decreased from 88% at 2 h to 65% at 12 weeks, while the methanol-soluble portion increased from 4.3% to 30% and the insoluble fraction increased slightly from 0.54% to 2.5% over the same period.

The methanol rinse (4.7% of the TRR) from the 12-week sample of peel was analysed by TLC and HPLC. OPP constituted 1.3% of the TRR or 0.12 mg/kg, and 2-methoxybiphenyl 0.3% or 0.025 mg/kg. No other compounds could be identified.

The methanol extract of the 12-week peel contained phenylhydroquinone at 2.8% of the TRR or 0.25 mg/kg, and OPP at 1.0% of the TRR or 0.093 mg/kg. All the components in the other bands or peaks, including 25% of the TRR at a 6-minute HPLC retention time, remained unidentified. All the other regions of radioactivity were individually <3% of the TRR. The hexane extract was found to contain only OPP, at 62% of the TRR or 5.7 mg/kg.

In an effort to identify the 6-minute HPLC peak in the methanol extract of the 12-week peel the extract from the high-dose peel was hydrolysed with 1 N HCl. The product mixture was extracted with ethyl acetate, which recovered 98% of the radioactivity. Analysis by TLC and HPLC revealed OPP and PHQ, in a ratio of 88:12 by HPLC. This corresponds to 26% of the TRR as OPP and 3.6% as PHQ. Presumably the increase in the OPP from 1% to 26% may be attributed to a conjugate hydrolysed by the acid.

The high-dose methanol extract was also hydrolysed with β-glucosidase. In the ethyl acetate extract of the hydrolysate, containing 58% of the radioactivity in the original methanol extract, OPP was the only significant compound, indicating that some of the OPP conjugation was with glucose.

The twelve-week post-extraction solid (2.5% of the TRR; 4.3% of the high-dose TRR) was hydrolysed successively with cellulase, 1 N HCl, and 25% NaOH. Cellulase released 0.64% of the TRR, acid released 0.41%, and NaOH released 1.0%. The hydrolysates were not investigated further.

The ethyl acetate extracts of the pulp and juice from the 12-week samples were analysed by HPLC and TLC. The major compound was OPP, representing about 76% of the radioactivity in the pulp extract (0.14% of the TRR, 0.01 mg/kg) and about 51% of that in the juice extract (0.12% of the TRR, 0.01 mg/kg).

The identified radiolabelled compounds in the 12-week peel are shown in Table 3.

Table 3. Compounds identified in the peel of oranges dipped in OPP solution and stored for 12 weeks.[1]

Compound	Methanol wash		Hexane extract		Methanol extract (including acid hydrolysate)		Total % of TRR identified	Total mg/kg identified
	% of fraction	% of TRR	% of fraction	% of TRR	% of fraction	% of TRR		
2-phenylphenol (OPP)	27	1.3	100	62	88	26	89	8.2
Phenyl hydro-quinone (PHQ)	-	-	-	-	22	3.6	3.6	0.33
2-methoxy biphenyl (2-MBP)	5.3	0.3	-	-	-		0.3	0.03
TOTAL							93	8.6

[1] The pulp and juice each contained 0.2-0.3% of the TRR, the major component of which was OPP.

In a metabolism study (Wu, 1995) a total of 153 pre-weighed Bosc pears were treated with a solution containing [^{14}C]SOPP labelled in the phenoxide ring plus unlabelled SOPP (Steri-Seal D) at a total concentration of 40 g/kg in sodium silicate solution (pear float) adjusted to pH 13.3 and maintained at 0˚C. The specific activity of the solution was 1,237 dpm/µg. A preliminary study had indicated that pears so treated and subsequently rinsed with water as recommended would contain a TRR of about 40 mg/kg OPP equivalent. All treated, rinsed pears were stored in sealed cabinets under controlled conditions of 90% humidity at 1-4ºC and eight pears were removed at intervals from 2 h to 28 weeks. Each pear was rinsed with 150 ml of methanol to remove surface residues and peeled. The combined peels were homogenized in liquid nitrogen and the peeled pears were cut into slices, combined and homogenized in liquid nitrogen. The TRR in each sample was measured.

The peel and pulp samples were extracted twice with 4:1 acetonitrile/0.1N HCl and the extracts partitioned twice with methylene chloride, giving methylene chloride/acentonitrile ($MeCl_2$/ACN) and aqueous fractions. The distribution of ^{14}C was determined in the initial rinse and in each extract by LSC and in the post-extraction solids (PES) by combustion. Initially 80% of the TRR was found in the rinse and 20% in the peel, with only 0.05% in the pulp. After storage, less radioactivity was found in the methanol rinse and more in the peel and pulp. The radioactivity in the pulp increased from 0.05% of the TRR at 2 h to 28% at 24 weeks, that in the peel increased to 66%, and that in the rinse decreased to 8.2%. Significant proportions of the radiolabel were translocated with time to both the peel and pulp.

The proportion of the TRR in the various extracts also changed with time. At 2 h after treatment the peel contained 20% (4.5 mg/kg as OPP), of which 95% was extracted into $MeCl_2$/ACN, 0.75% was in the water and 3.9% remained in the PES. After 28 weeks the peel contained 66% of the

TRR (27.7 mg/kg) of which 80% was extracted into the $MeCl_2$/ACN fraction, 10% was in the aqueous fraction and 9.2% was in the PES.

The pulp of pears stored for less than 4 weeks contained only low levels of radioactivity. At 8 weeks it contained 7.6% of the TRR (2.9 mg/kg as OPP), of which 39% was extracted into $MeCl_2$/ACN, 59% was in the aqueous extract and 1.8% was in the PES. At 28 weeks, the pulp contained 26% of the TRR (11 mg/kg OPP equivalent), of which 56% was in the $MeCl_2$/ACN extract, 44% in the aqueous fraction and 2.0% in the PES.

The post-extraction solid from the 28-week peel was sequentially hydrolysed with cellulase (37˚C, 24 h), 1 N HCl (110˚C, 2 h) and 6 N HCl (110˚C, 24 h). Each product mixture was partitioned between water and ethyl acetate.

The methanol rinse and all the $MeCl_2$/ACN and aqueous extracts from the peel and pulp were examined by reversed-phase HPLC, with detection by UV (254 nm) and flow-through radioactivity detectors. Fractions were also collected at timed intervals and analysed by LSC. TLC on normal-phase silica gel plates was used for confirmation of identities and for purification of fractions. Developed plates were scanned with a bio-imaging analyser. Reference standards included 4,4'-biphenyldiol, phenylhydroquinone (PHQ), 2,2'-biphenyldiol, phenyl-1,4-benzoquinone, 2-phenylphenol (OPP), 2-methoxybiphenyl (2-MBP) and dibenzofuran. GC-MS with a double-focusing magnetic sector instrument operated in the electron-impact mode was used for the qualitative identification of some metabolites. Thermospray LC-MS was also used to analyse the rinse and the hydrolysate of the 28-week post-extraction solid of the peel for non-polar metabolites.

The findings are shown in Table 4. Metabolites A, B, C, D, E, F and G were identified as conjugates of OPP by isolation of each metabolite, acid hydrolysis, and analysis of the hydrolysate extract. They are most likely to be sugar conjugates. Dibenzofuran, 4,4'-biphenyldiol, 2,2'-biphenyldiol and phenyl-1,4-benzoquinone were not detected in any extract.

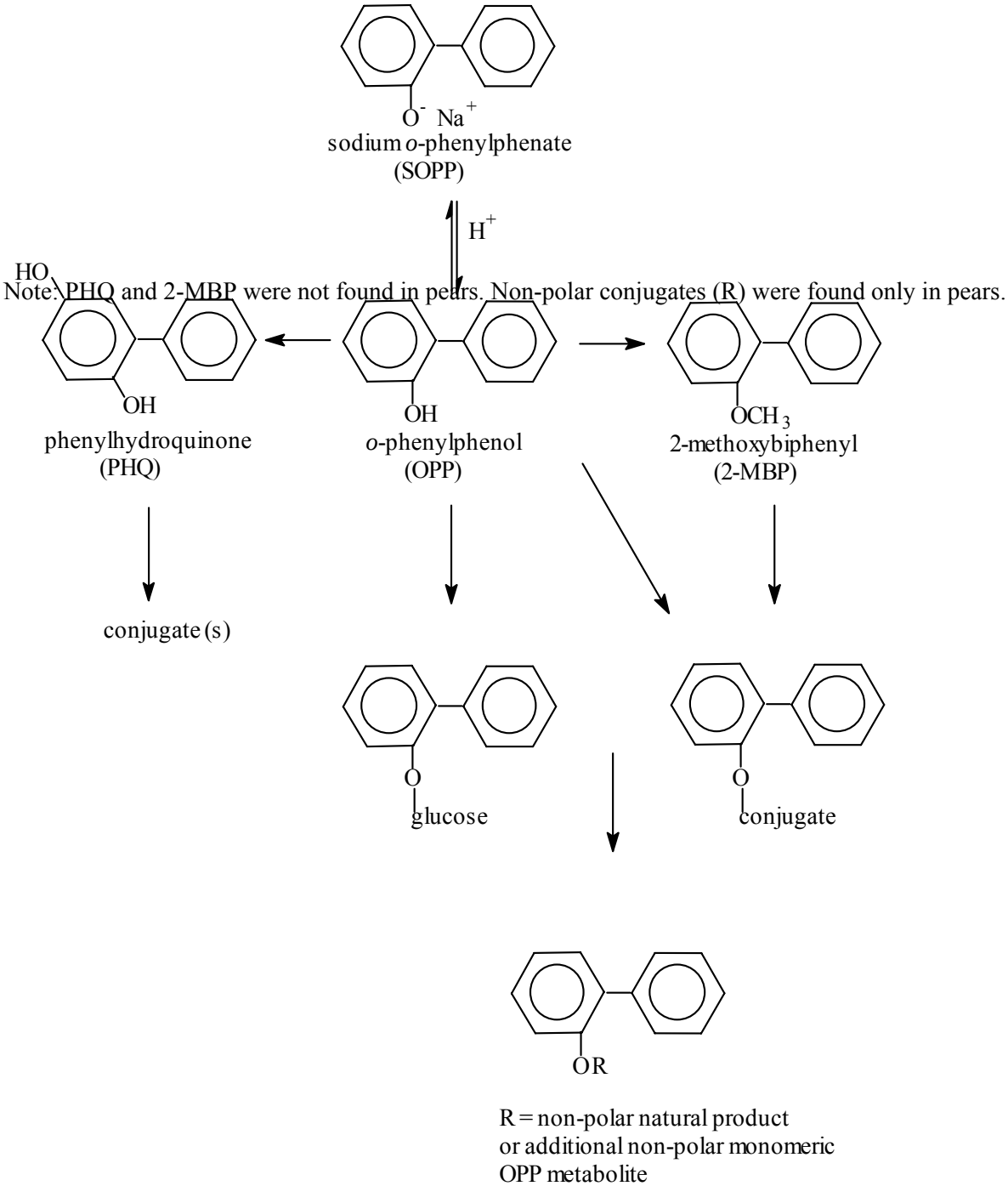
Table 4. Identification of compounds in extracts of pears dipped in OPP and stored for 28 weeks.

Sample	OPP		Metabolites A-F[1]		Metabolite G[2]		Total identified	
	% of TRR	mg/kg[3]	% of TRR	mg/kg[3]	% of TRR	mg/kg[3]	% of TRR	mg/kg[3]
PEEL								
$MeCl_2$/ACN extract	3.2	1.4	44	18			47	19
Aqueous extract			6.8	2.9			6.8	2.9
EtOAc extract of PES cellulase hydrolysate			0.28	0.12	2.9	1.2	3.2	1.3
PULP								
$MeCl_2$/ACN extract	0.49	0.21	14	4.5			14	4.7
Aqueous extract			12	4.9			12	4.9
RINSE	2.6	1.1	1.3	0.56			3.9	1.7
Total	6.3	2.7	78	31	2.9	1.2	87	35

[1] Structures of metabolites A-F were consistent with OPP conjugates.
[2] Metabolite G was isolated from the ethyl acetate extract of the cellulase hydrolysate of the post-extraction solid. It was hydrolysed with 1 N HCl, purified, and examined by HPLC. The single peak corresponded to OPP. The purified G was also examined by LC-MS. The fragment ions were consistent with a glucose conjugate of OPP.
[3] Expressed as OPP.

The metabolism of OPP by oranges and pears is consistent with the pathways shown in Figure 2. In oranges the radiolabelled residue showed no tendency to be translocated beyond the peel. After 12 weeks 95% of the total radioactive residue was in the peel 89% as OPP and 4% as PHQ. Less than 0.5% of the TRR was in the pulp and 76% of that was OPP. The situation was different with pears, where a significant proportion of the TRR was found in the pulp. After 24 weeks 28% of the total radioactive residue was in the pulp, 50% of which was OPP and its conjugates. No PHQ was found.

Figure 2. Metabolic pathways of OPP in pears and oranges.



Note: PHQ and 2-MBP were not found in pears. Non-polar conjugates (R) were found only in pears.

Environmental fate in soil

OPP is not directly applied to the soil or to planted crops. Its use is for the post-harvest treatment of fruit. No studies were reported, but a review of the breakdown of OPP in soil was provided (Zbozinek, 1984). It is noted that exact information on the specific pathways of OPP metabolism by micro-organisms in soil is lacking, but it is postulated that the breakdown is similar to known pathways for biphenyl. OPP would be oxidized to 3-phenylcatechol which, by analogy with biphenyl, would be converted to acetaldehyde, pyruvate and benzoate. A different pathway involves transformation of OPP into stable polymers which eventually become part of the humus.

Environmental fate in water/sediment systems

The biodegradation of OPP in river water and activated sludge was studied by Gonsior *et al*. (1984). OPP was degraded completely within 2 days in a simulated biological wastewater treatment system at concentrations of 30 and 100 mg/l, but the antimicrobial properties of OPP slowed its degradation at concentrations above 100 mg/l. The biodegradability of OPP at concentrations expected to be found in the environment was determined with [^{14}C]OPP uniformly labelled in the phenolic ring at concentrations of 123, 12.3 and 1.22 µg/l in water from the Tittabawassee river (Midland, MI), at 20ºC in the dark. Analysis by HPLC at intervals showed a reduction to half the initial concentration within about 1 week. The $^{14}CO_2$ reached 50% of its theoretical maximum after 16 days. After 30 days incubation with $HgCl_2$ added to inhibit biological activity, [^{14}C]OPP accounted for about 79% of the initial radioactivity in the river water sample; about 8% was from breakdown products extractable with methylene chloride and <0.2% had been converted to $^{14}CO_2$.

The rate of degradation of [^{14}C]OPP was also studied at an initial concentration of 9.6 mg/l in activated sludge obtained from a wastewater treatment plant. A reduction to half the initial concentration was found within 24 and 3 hours in fresh sludge and sludge pre-treated for 6 days with unlabelled OPP respectively. The $^{14}CO_2$ evolved in 48 hours was two-thirds of the theoretical maximum production in both experiments.

In a 1997 study using a modification of the OECD Method 301B biodegradability test, [^{14}C]OPP uniformly labelled on the phenolic ring was added at nominal concentrations of 0.2 and 1.0 mg/l to a mineral medium with a microbial inoculum from a municipal wastewater treatment plant. The concentration of suspended solids in the mixed liquor was 30 mg/l. The low concentrations of test material were needed to avoid potential inhibitory effects upon the micro-organisms. Extensive biodegradation of OPP was observed at 23ºC in the dark: by day 11, two-thirds of the ^{14}C added to the reaction mixtures was converted to $^{14}CO_2$. This met the guideline criterion for classification as readily biodegradable (60% of the theoretical $^{14}CO_2$ production obtained within a 10-day window in the 28-day test). The recovery of radioactivity after 28 days ranged from 76% from the killed controls to 87-88% from the biologically active mixtures. In the active reaction mixtures, mineralization to $^{14}CO_2$ accounted for 72-76% of the radioactivity, while 6-7% was incorporated into the biomass or adsorbed onto the solids and 6-8% remained in solution. Since <1% of the radioactivity was evolved as $^{14}CO_2$ in the killed controls, the mineralization was biologically mediated (Gonsior and Tryska, 1997).

METHODS OF RESIDUE ANALYSIS

Analytical methods

The government of The Netherlands supplied a reference to its official method for the determination of OPP (Ministry of Health, Welfare and Sport, 1996). An extract is analysed by GLC with an ion trap detector. Details were not provided. The limit of determination was stated to be 0.01-0.05 mg/kg, and the recovery from various commodities at 0.12 mg/kg to be 99%.

The colorimetric method 180.129 of the US Food and Drug Administration (FDA Pesticide Analytical Manual, 1987) determines OPP and its sodium salt in tomatoes, sweet potatoes and fresh

pineapples with an estimated limit of detection of 3 mg/kg. A 500 g sample is chopped and steam-distilled in 400 ml of water and 100 ml of 85% phosphoric acid. A known volume of the distillate is adjusted to pH 10.3-10.5 and diluted to 190 ml with sodium carbonate buffer. 4-Aminoantipyrine solution (2%, 1 ml) and potassium ferricyanide solution (2%, 1 ml) are added and the volume is adjusted to 200 ml. The absorbance at 500 nm is read after 7-10 minutes. Calibration is by external standards.

In a modification of the US FDA method (Smith, 1999) the distillate, without pH adjustment, is analysed by HPLC with a UV detector (280 nm). The eluant is methanol/water (65:35). No additional details were provided. The method was used for the determination of OPP in pear peel. Calibration was by external standards (0.025-0.50 mg/kg).

Another variation of the FDA procedure was applied to the analysis of citrus fruit by Tanaka *et al.* (1978). Five fruits are chopped and slurried, and 80 g of the slurry is mixed with 70 ml of distilled water, 10 ml heptane and 2 ml sulfuric acid. The mixture is steam-distilled and the distillate collected in traps of 15% sodium hydroxide. The solution in the traps is diluted with water to 500 ml and a 5 ml portion is neutralized and derivatized with pentafluorobenzoyl chloride. The reaction mixture is extracted with heptane and the extract together with 1,1-dichloro-2,2-bis(4-chlorophenyl)ethylene as internal standard, is analysed by GLC with an electron capture detector. The recoveries of OPP from lemons, oranges and grapefruit at fortifications of 5 and 10 mg/kg were 95-99%.

A GLC method for the determination of OPP residues in citrus fruit, kiwifruit and cantaloupes was supplied by Elf Atochem (1990). A mixture of 330 g slurried fruit, 15 ml concentrated HCl, antifoam drops, and 14 ml hexane is refluxed for 1.5 hours and distilled. The distillate is made alkaline with 5 N NaOH and partitioned with hexane after adding salt. The aqueous layer is adjusted to pH 2.0 with HCl and extracted with hexane. The final hexane extract is analysed by GLC with a 15 m x 0.53 mm DB-1 column and a flame ionization detector. Calibration is with external standards. The limit of determination is 0.10 mg/kg.

Several HPLC methods are described in the literature (Reeder, 1976; Farrow *et al.*, 1977; Ott, 1978). The most recent version was provided by Sunkist Growers, Inc. (1999). The method has been applied to Navel and Valencia oranges, lemons, tangerines, tangelos, mandarins, minneolas, pummelos and pink and white grapefruit to determine OPP, imazalil and thiabendazole. Ten or 12 fruits are cut into 6 sections each and one section is taken from each fruit. The composite samples (300-350 g) are separated into peel and fruit sacs. The peels are slurried in a blender with ethyl acetate (200 ml), the slurry is filtered and the grinding and filtering process is repeated twice. The extract is analysed by HPLC on a Zorbax ODS, 250 cm x 4.6 mm, column with 30.2% phosphate buffer and 69.8% acetonitrile as the mobile phase at a flow of 1 ml/min. A fluorescence detector with a 254 nm excitation filter is used with calibration by external standards (0.25-3.8 mg/kg). The linear calibration curve is based on duplicate injections at each concentration. The limit of detection is estimated to be 0.05 mg/kg OPP and the limit of determination assumed to be 0.25 mg/kg.

A GC-MS method, validated with radiolabelled compounds, was described for the determination of OPP and the metabolite PHQ (phenylhydroquinone) in citrus fruits and their processed fractions (Harsy, 1996a) and submitted as a proposed enforcement method to the US EPA. Fruit samples are cut into small pieces and ground in liquid nitrogen. Juice samples are frozen as received. To determine OPP, thawed homogenate or juice (10 g) is simultaneously hydrolysed, steam distilled and extracted in a micro-Nielsen-Kryger apparatus, using sufficient HCl to produce a 1 N concentration in the sample. Water and iso-octane are placed in the inner chamber of the apparatus. The mixture is refluxed for 2 hours (pulp overnight). The OPP is derivatized with *N,O*-bis(trimethylsilyl)trifluoroacetamide (BSTFA) to form the trimethylsilyl ethers and determined by GC-MS in the selected ion mode. The ions 227, 242, 170 and 141 are monitored, with a dwell time of 50 msec per ion. The column is a 30 m x 0.25 mm HP-5 (5% phenyl methyl silicone). The ion m/z

227 is used for quantification with external standards. Orange oil is determined by direct injection, monitoring ion m/z 170.

For the determination of PHQ, the homogenized sample or juice (10 g) is hydrolysed in 0.3 N HCl with ascorbic acid and EDTA for one hour at 100˚C under argon. The mixture is extracted with methylene chloride and the PHQ derivatized with BSTFA (70˚C, 15 min). The derivative is determined by GC-MS, monitoring ions 330 and 229, the former being used for quantification.

Both OPP and PHQ standards showed linear detector response from 0 to 6 or 7 ng injected on the column.

The LOD was 0.05 mg/kg for OPP and 0.2 mg/kg for PHQ in all samples except oil, in which it was 1 mg/kg for both compounds. Some recoveries are shown in Table 5.

Table 5. Recoveries of OPP and PHQ from fortified citrus fruit by GC-MS.

Analyte and sample	Fortification, mg/kg	Mean recovery, %	Number of samples	Range, %	Standard deviation, %
OPP					
Orange	0.05	118	8	104-126	7.0
	1	80	2	78, 82	-
	20	74	2	74, 75	-
Lemon	0.05	92	7	80-104	7.1
	1	65	2	65, 65	-
	20	77	2	76, 77	-
Juice	0.05	88	8	83-93	3.8
	1	96	2	94, 97	-
	20	80	2	80, 80	-
Pulp, dry	0.05	82	8	77-88	3.9
	1	70	2	69, 71	-
	20	93	2	74, 112	-
Oil	0.05	76	8	74-78	1.4
	10	63	2	60, 65	-
	30	71	2	70, 71	-
PHQ					
Orange	0.2	78	8	72-85	4.1
	1	82	2	79, 85	-
	20	83	2	76, 89	-
Lemon	0.2	76	7	65-84	6.0
	1	78	2	78, 78	-
	20	104	2	99, 108	-
Juice	0.2	76	8	69-81	3.8
	1	77	2	77, 78	-
	20	65	2	64, 65	-
Oil	1	76	8	72-79	2.2
	3	66	2	65, 67	-
	5	65	2	64, 66	-
	10	73	2	73, 73	-

The method was validated (Harsy, 1996b) with a 12-week peel sample from the orange metabolism study which contained a total radioactive residue of 28.68 mg/kg as OPP. Analysis of the residue showed it to be 89% OPP and conjugates and 3.6% PHQ and conjugates (see Table 3), giving a residue of OPP and its conjugates of 25.5 mg/kg and PHQ and conjugates of 1.0 mg/kg. The peel was analysed by the GC-MS method and the results compared with those from the metabolism study (Table 6).

Table 6. Validation of the GC-MS method with orange peel containing incurred residues of 25.5 mg/kg [^{14}C]OPP and conjugates and 1.0 mg/kg [^{14}C]PHQ and conjugates.

Sample	OPP recovery, %	Total radioactivity - OPP, %	PHQ recovery, %	Total radioactivity - PHQ, %
Peel replicate 1 extract	84	74	109	73
Peel replicate 1 residue		32		20
TOTAL replicate 1		106		93
Peel replicate 2 extract	85	76	111	77
Peel replicate 2 residue		38		19
TOTAL replicate 2		114		96

Stability of pesticide residues in stored analytical samples

The storage stability of OPP and PHQ in raw oranges, grapefruit and lemons, and processed orange products was studied by Johnson and Strickland (1996a-c). Samples of whole grapefruit, lemons, and navel oranges, and navel orange juice, oil and dry pulp were fortified with OPP and PHQ, each at 0.5 mg/kg, and held in frozen storage. Samples were removed at intervals and analysed for OPP and PHQ by the Harsy GC-MS method. Fortified controls were analysed at each interval to establish method recoveries. The results are shown in Table 7. OPP was stable in grapefruit for 6 months, in lemons for 8 months, in oranges for 7 months, in juice for 5 months, in dried pulp for 4 months and in oil for 9 months. PHQ was stable in grapefruit for 5 months and in orange juice for 5 months, but unstable in oranges and oil. The stability in lemons is uncertain, because the concurrent method recoveries were very poor.

Table 7. Recoveries from stored and freshly fortified samples of citrus fruits and processed orange commodities fortified with OPP and PHQ, each at 0.5 mg/kg (10.5 mg/kg in citrus oil) and stored frozen at -20˚C.

Commodity	Storage period, months[1]	Recovery from freshly spiked samples, %[2]	Recovery from stored samples, %	% of mean fresh recovery after storage
OPP				
Grapefruit	1.0	64, 69 (66)	59, 66	89, 100
	1.9	70, 73 (71)	67, 76	94, 106
	2.8	73, 74 (74)	72, 73	97, 99
	3.8	147, 154 (151)	128, 141	85, 93
	5.9	82, 83 (82)	80, 84	97, 102
Lemons	0.2	93, 119	-	-
	1.00	103, 124 (113)	148, 153	130, 135
	1.9	114, 124 (119)	64, 119	54, 100
	3.1	84, 86 (85)	103, 109	121, 129
	4.1	68, 69 (68)	88, 91	129, 133
	8.4	78, 82 (80)	104, 108	130, 135
Oranges	1.0	56, 59 (58)	71, 74	103, 105
	2.1	69, 69 (69)	71, 72	103, 105
	3.1	83, 84 (84)	75, 85	90, 101
	4.0	70, 79 (75)	73, 76	97, 101
	5.2	148, 155 (151)	123, 142	81, 94
	7.2	76, 77 (77)	80, 83	105, 108
Juice	1.2	77, 88 (82)	79, 82	96, 99
	2.4	72, 72 (72)	76, 78	106, 108
	3.2	85, 153 (119)	81, 89	68, 75
	4.3	79, 83 (81)	82, 87	102, 108
	5.3	141, 150 (145)	145, 146	100, 101
Dried pulp	3.6	71, 72 (72)	68, 73	95, 102
	4.0	94, 150 (122)	123, 141	101, 115

Commodity	Storage period, months[1]	Recovery from freshly spiked samples, %[2]	Recovery from stored samples, %	% of mean fresh recovery after storage
	6.2	46, 53 (49)	39, 48	79, 97
Oil[3]	0	52, 54 (53)	-	-
	0.9	84, 87 (86)	88, 90	102, 105
	1.9	74, 84 (79)	83, 81	105, 102
	4.5	82, 87 (84)	84, 80	100, 95
	5.0	90, 92 (91)	90, 92	99, 101
	6.1	114, 111 (112)	108, 106	96, 95
	7.7	99, 102 (100)	96, 105	96, 105
	9.1	83, 86 (84)	89, 91	106, 108
PHQ				
Grapefruit	3.4	53, 102 (77)	82, 131	106, 171
	4.8	80, 87 (83)	87, 87	104, 104
	6.1	47, 54 (50)	50, 53	101, 105
	9.4	36, 40 (38)	42, 43	111, 113
Lemons	7.5	31, 88 (60)	136, 171	228, 287
	8.6	23, 33 (28)	40, 44	143, 156
	9.8	31, 32 (31)	49, 59	155, 187
Oranges	3.2	67, 78 (72)	38, 55	52, 76
	4.7	42, 76 (59)	19, 71	32, 121
	5.8	81, 81 (74)	50, 59	62, 72
	7.5	67, 81 (74)	16, 32	22, 44
Juice	1.9	78, 79 (78)	73, 92	92, 116
	3.2	61, 66 (63)	74, 84	116, 132
	4.7	75, 78 (77)	77, 79	101, 103
Oil	0	71, 75 (73)	-	-
	0.9	94, 103 (99)	41, 51	41, 52
	1.9	61, 59 (60)	<10, <10	<17, <17
	2.5	95, 98 (97)	<10, <10	<10, <10

[1] Initial samples, except of oil, were not analysed.
[2] Values in parenthesis are means of two independently fortified and analysed fresh control samples.
[3] Control samples contained significant concentrations of OPP (1.2-2.1 mg/kg). Results were corrected.

Definition of the residue

The current definition is "sum of 2-phenylphenol and 2-phenylphenate, expressed as 2-phenylphenol".

In studies of metabolism in oranges and pears OPP and its conjugates constituted 90% of the total radioactive residue (TRR) in oranges and 87% of the TRR in pears. PHQ was found in orange peel at low concentrations (<4% of the TRR). It is therefore appropriate to define the residue for both enforcement and for the estimation of dietary exposure as the sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol. This applies to plant commodities only.

USE PATTERN

Information was supplied by the California Citrus Quality Council (CCQC), the Pear Bureau Northwest and the governments of Australia, The Netherlands and Germany. Germany and The Netherlands indicated that they had no registered uses. The only uses are for the post-harvest treatment of citrus fruit and pears, most commonly to control green mould and sour rot. The information is shown in Table 8.

Table 8. Registered uses of 2-phenylphenol.

Crop	Country	Formulation	mg ai/kg fruit or solution concen-tration, kg ai/hl	Method	Comments
Citrus	Australia	SP, 950 g/kg	1.9 (as Na OPP tetrahydrate)	Dip	Adjust dip pH to 12. Wash fruit after dip.
Citrus	USA	Wax liquid with 0.40% OPP	4.2 mg/kg fruit	Spray	Spray without dilution on to clean and dry citrus, 1 gal (8.5 lbs) per 8000 lbs fruit
Citrus	USA	SC, 25% SOPP	0.97 kg ai/hl 8.1 mg ai/kg fruit	Wax emulsion	Use wax foamer or sprayer. Do not rinse.
Citrus	USA	Foaming cleaner, 14.5% SOPP; 24% SOPP	1.6 (as Na OPP) 2.0 (as Na OPP tetrahydrate)	Mechanical foamer or spray	10-30 second treatment with 14.5% followed by fresh water rinse. For 14.5%, dilute 1 gal with 9 gal water. 1 gal = 9.0 lbs . 30-60 second treatment for 24%, followed by a water rinse. 1 gal = 3.1 lbs. Na OPP tetrahydrate.
Citrus	USA	SC, 14.5% anhydrous Na OPP	0.05 (500 ppm)	Bin drench	Dilute with water. 1 gal = 8.93 lbs.
Citrus	USA	SC, 14.5% SOPP anhydrous; 25% SOPP tetrahydrate	0.34 (3500 ppm) for SOPP anhydrous; 0.5 for SOPP tetrahydrate	Washing tank.	Wash in tank 2-5 minutes, after adjusting pH to >11.6. Wash citrus after treatment with fresh water. For 14.5%, 1 gal = 9.18 lbs. Dilute 1 gal with 46 gal water minimum. For 25%, 1 gal = 3.33 lbs. SOPP tetrahydrate. Dilute 1 gal with 80 gal water.
Pears	USA	Foaming cleaner, 14.5% SOPP; 24% SOPP	1.3 (as Na OPP) 1.9% (as Na OPP tetrahydrate)	Mechanical foamer or spray	For 14.5%, dilute 1 gal with 11 gal water. Foam and brush onto pears for 15-30 seconds. Rinse with fresh water. 1 gal = 9.0 lbs. For the 24%, dilute one gallon with 19 gallons of water. Treat for 15-30 seconds. 1 gal = 3.1 lbs. SOPP tetrahydrate.
Pears	USA	SC, 14.5% SOPP anhydrous; SC, 25% SOPP	0.35 (3500 ppm) for 14.5%; 0.5 for 25%	Dip	For 14.5%, add 1 gal to 44 gallons of water. Dip for 1.5 to 4 minutes and then rinse thoroughly with fresh water. 1 gal = 9.18 lbs. For 25%, add 1 gal to 80 gal water, adjust pH to 11-12, dip or flood for 0.5-2 min and rinse. 1 gal = 3.33 lbs SOPP tetrahydrate.

RESIDUES RESULTING FROM SUPERVISED TRIALS

In 8 US trials (Johnson and Strickland, 1996) commercially grown citrus fruit from southern California (lemons, Navel oranges and grapefruit) and central Florida (grapefruit) were treated with SOPP. Scarred fruit were used, as they tend to show higher residues of OPP. Lemons were treated with a storage wax containing 2,4-D and imazalil and stored at 7-18˚C for six weeks before the trial. Navel oranges and grapefruit were treated with SOPP within four days of harvest.

Lemons, oranges and grapefruit were given a foamer wash treatment for 30 seconds with a solution containing 1.45% anhydrous SOPP (2.0% SOPP tetrahydrate), followed by a fresh water rinse. The label specifies 1.6 kg ai/hl as anhydrous SOPP. A sample of the treated fruit was collected immediately after the water rinse. Control samples received a foaming wash without OPP.

The foamer wash experiments were conducted in duplicate with individually prepared solutions. The foamer wash solution is applied as a high-volume flush over the fruit as it moves across a series of parallel brushes that generate the foam. The application rate is dependent on the time spent on the brushes and not the volume output of the sprayer, provided the brushes are thoroughly soaked.

The remaining fruit from the foaming wash/water rinse were treated with a shipping wax that contained 1.0% anhydrous SOPP. The treatment was in duplicate with individually prepared wax solutions. GAP specifies approximately 1 kg ai/hl, or 1%. The wax was applied with a bank of parallel stiff brushes that carried fruit under a pair of ultra low volume spray heads or under a wax drip system which kept the brushes saturated with wax. The pumps supplying the wax were adjusted to deliver it at one gallon of wax solution per 10000 pounds of fruit, as specified by the label.

The samples which had not received the wax treatment were frozen on the day of treatment and kept frozen until analysis, a period of 1-8 months. The remaining control and foam-treated samples which received the wax treatment were placed in storage that simulated commercial conditions. Lemons were stored at temperatures of 10-11˚C and relative humidities of 96-97%. Navel oranges were stored at 5.5-10.5˚C and relative humidities of 75 to 84%. California grapefruit were stored at 5-11˚C and relative humidities of 71 to 83%, and Florida grapefruits at 12-15˚C and 74 to 98%. Samples were taken after 4 and 8 weeks and frozen until analysis. The usual interval between post-harvest SOPP treatment and citrus consumption is estimated to be 8 weeks.

The fruit samples were analysed by the Harsy method (one-step hydrolysis/steam distillation/extraction, followed by GC-MS). Both OPP and PHQ were determined. The results are shown in Table 9. Fortified control samples were analysed concurrently with the results shown in Table 10.

Table 9. OPP and PHQ residues in oranges, lemons and grapefruit treated with 1.45% anhydrous SOPP foamer wash and 1.00% anhydrous SOPP in shipping wax.

Trial no. (site)	Treatment and storage period, days							
	Foamer wash (day 0)		Foamer wash + wax (day 0)		Foamer wash + wax (day 28)		Foamer wash + wash (day 56)	
	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg
Navel oranges								
1	1.7, 1.4 (1.6)	<0.2, <0.2	7.0, 6.4 (6.7)	<0.2, <0.2 (<0.2)	5.8, 7.0 (6.4)	<0.2, <0.2 (<0.2)	4.9, 6.1 (5.5)	0.27, 0.33 (0.30)
2	1.8, 1.5 (1.6)	<0.2, <0.2 (<0.2)	6.2, 6.8 (6.5)	<0.2, <0.2 (<0.2)	5.7, 6.0 (5.8)	<0.2, <0.2 (<0.2)	6.5, 6.4 (6.4)	0.25, 0.26 (0.26)
Control	<0.05	<02	0.057	<0.2	0.083	<0.2	0.066	<0.2
Lemons								
1	2.4, 2.7 (2.6)	<0.2, <0.2 (<0.2)	4.5, 3.8 (4.2)	<0.2, <0.2 (<0.2)	4.6, 5.2 (4.9)	0.34, 0.34 (0.34)	4.9, 5.9 (5.4)	0.34, 0.31 (0.32)
2	3.4, 3.2 (3.3)	<0.2, <0.2 (<0.2)	4.5, 4.6 (4.6)	<0.2, <0.2 (<0.2)	5.8, 4.8 (5.3)	0.32, 0.35 (0.34)	5.0, 5.3 (5.2)	0.33, 0.40 (0.36)
Control	<0.05	<0.2	0.062	<0.2	0.062	<0.2	0.077	<0.2
Grapefruit								
1 (Calif)	1.1, 0.73 (0.91)	<0.2, <0.2 (<0.2)	1.9, 2.3 (2.1)	<0.2, <0.2 (<0.2)	2.3, 1.9 (2.1)	0.47, 0.44 (0.46)	3.5, 1.3 (2.4)	0.50, 0.23 (0.36)
2 (Calif)	1.3, 1.7 (1.5)	<0.2, <0.2 (<0.2)	2.4, 2.1 (2.2)	<0.2, <0.2 (<0.2)	2.1, 2.5 (2.3)	0.47, 0.37 (0.42)	2.5, 2.4 (2.4)	0.49, 0.40 (0.44)
Control (Calif)	<0.05	<0.2	<0.05	<0.2	<0.05	<0.2	<0.05	<0.2
3 (Florida)	0.31, 0.48 (0.40)	<0.2, <0.2 (<0.2)	3.4, 2.0 (2.7)	<0.2, <0.2 (<0.2)	1.8, 1.6 (1.7)	<0.2, <0.2 (<0.2)	1.9, 1.4 (1.7)	0.21, <0.2 (0.21)

Trial no. (site)	Treatment and storage period, days							
	Foamer wash (day 0)		Foamer wash + wax (day 0)		Foamer wash + wax (day 28)		Foamer wash + wash (day 56)	
	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg	OPP, mg/kg	PHQ, mg/kg
4 (Florida)	0.65, 0.83 (0.74)	<0.2, <0.2 (<0.2)	2.0, 2.4 (2.2)	<0.2, <0.2 (<0.2)	2.2, 1.6 (1.9)	<0.2, <0.2 (<0.2)	3.0, 1.8 (2.4)	0.46, 0.22 (0.34)
Control (Florida)	<0.05	<0.2	0.063	<0.2	<0.05	<0.2	<0.05	<0.2

Table 10. Recovery of OPP and PHQ from fortified citrus samples analysed concurrently with the treated samples of Table 9.

Analyte and sample	Fortification, mg/kg	Number of samples	Recovery range, %	Mean recovery, %
OPP				
Orange	0.05	4	80-99	86
	0.5	5	58-104	72
	1	5	69-95	84
	5	4	69-95	88
Lemon	0.25	5	73-93	83
	0.5	2	74, 78	76
	1	9	69-93	80
	5	2	81, 109	95
Grapefruit (California)	0.05	3	97 - 139	119
	0.5	6	68-99	86
	1	5	73-99	90
	5	4	70-101	86
Grapefruit (Florida)	0.05	4	89-105	96
	0.5	4	66-74	71
	0.25	1	104	-
	1	5	88-101	93
	5	4	78-92	85
PHQ				
Orange	0.2	9	55-117	85
	1	9	54-119	86
Lemon	0.2	9	64-93	78
	1	9	61 - 96	77
Grapefruit (California)	0.2	9	68-95	80
	1	9	66-95	78
Grapefruit (Florida)	0.2	9	60-125	77
	1	9	61-118	80

Two trials at the same location with the same equipment, but with two independently prepared treatment solutions, were conducted with Anjou pears in Oregon, USA, in 1995 (Thompson, 1996). Pears after 4 months cold storage were dipped in a float tank for 120 seconds in a solution containing 0.49% SOPP (Steriseal D, 24.4% anhydrous SOPP by analysis, nominal 22.6% on label). The pears were rinsed under flowing water and dried briefly with a hair dryer. This is consistent with US GAP. Controls were dipped in a solution that did not contain SOPP. In each trial, a 4.54 kg sample of pears was collected and a 2.27 kg sub-sample was frozen within 3 h (day 0). In one trial the remaining 2.27 kg of fruit was divided into two sub-samples, which were stored at -2 to 2ºC and >90% relative humidity for 60 or 120 days. In the other trial the remaining 2.27 kg was again divided into two portions, which were stored under controlled conditions at -1 to 0ºC and 90-95% relative humidity for 60 or 113 days. The samples were all immediately frozen and kept frozen until analysed. The maximum interval from sampling to analysis was about 6 months for the day 0 samples and correspondingly less for the samples stored before freezing.

Storage stability studies showed acceptable or marginally acceptable recoveries at all intervals up to 4 months, but recoveries from the 6-month samples were below 50%, suggesting that the initial trial samples (stored frozen for 6 months) may have contained twice the measured residues. It is also to be noted that the stability study was with a pear homogenate, not with whole fruit. A freshly fortified sample was not analysed with each set of stored samples to provide information on analytical recoveries. The results of the storage stability trials are shown in Table 11.

Table 11. Recovery of OPP from fortified pear homogenate after frozen storage.

Storage period, days	Fortification, mg/kg	Recovery, %[1]
0	1.18	79
	18.1	100
30	1.51	57
	17.9	70
60	1.50	78
	19.9	106
120	1.50	83
	24.8	109
210	1.51	43
	15.5	44

[1] Not corrected for concurrent analytical recovery

Samples and controls were analysed by the Harsy GC-MS method. All residues in control samples were below the LOD (<0.15 mg/kg). Fortified controls (12 determinations) gave recoveries ranging from 71% to 103% at fortification levels of 0.1-15 mg/kg. The residues in the treated samples are shown in Table 12.

Table 12. Residues of OPP on pears after a dip treatment for 120 seconds in a 0.49% aqueous solution of SOPP.

Trial	Post-treatment storage period, days	OPP, mg/kg
1	0	1.7, 1.1 (Mean 1.4)
	60	0.93, 1.5 (Mean 1.2)
	120	0.69, 1.0 (Mean 0.87)
2	0	0.85, 0.79 (Mean 0.82)
	60	0.82, 0.74 (Mean 0.78)
	120	0.70, 0.57 (Mean 0.63)

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information, except on stability in stored analytical samples.

In processing

In a processing study (Johnson and Strickland, 1996) commercially grown Navel oranges from Tulare County, California, were scarified before an exaggerated treatment with a foamer wash solution

containing SOPP at 14.5 g/kg (or SOPP tetrahydrate at 20 g/kg) for 120 sec rather than the usual 30 sec. This was followed by application of a shipping wax solution containing SOPP at 10 g/kg (14 g/kg as SOPP tetrahydrate), thiabendazole at 3500 mg/kg and imazalil at 2000 mg/kg. Control samples received similar treatments with foamer wash and shipping wax solutions containing no SOPP. Two lots of each treatment solution were prepared for duplicate applications. A sample weighing about 50 kg was collected from control and treated oranges after storage periods of 0, 28 and 56 days and 4.5 kg of each initial sample was selected randomly to produce two 1.4 to 1.8 kg sub-samples, which were frozen immediately and shipped frozen to the laboratory for analysis.

The remaining 45 kg of each of the initial samples was sent to an experimental processing facility and processed into juice, dry pulp and oil. Two sub-samples were randomly selected from the whole fruit and from each process fraction. Two replicates from each sub-sample were frozen immediately for analysis for OPP and PHQ.

The remaining control and treated samples were placed in commercial storage for 28 or 56 days (5-10˚C, 75-84% relative humidity), then treated in the same way as the initial samples.

The raw oranges were processed by simulated standard industrial procedures. After washing for five minutes substandard fruits were removed by hand and the remainder (5-10 kg) were scarified for 0.5-5 minutes in a modified vegetable peeler, simulating the Brown Machinery commercial procedure. The collected flavedo and oil/water emulsion were passed through a 180 μm mesh screen to remove flavedo fragments and the emulsion was broken by freezing. After thawing, the floating oil was centrifuged at 2600 rpm for 10 minutes to effect the final separation of pure oil. In a commercial operation the emulsion would be screened and centrifuged at 10000 rpm.

The scarified oranges were transferred to a Hollymatic juice extractor which halved the fruit and then used auger reamers to remove the juice from the halves. This simulates closely the Brown Machinery juice extractor used commercially. The extracted juice was passed through a pulper finisher with a 0.4-0.6 mm screen to remove the vesicular membranes, seeds, segment membranes and peel fragments.

In commercial operations, most peel and rag from the juicer and finisher are sold as fresh or dried animal feed. The peel may also be used to make specialized products such as pectins, essential oils, candied peel, marmalade and citrus molasses. In the laboratory procedure, the flavedo from the scarification process (to produce oil) and the rag and seeds from the juice and finisher extraction processes were added to the shredded peel to produce wet pulp.

Citrus molasses is produced by reacting the peel with lime, pressing the peel to extract the juice and concentrating the juice. In the present study the wet pulp was mechanically shredded and lime was added to a pH of 8-10 and mixed for 15-20 minutes. The pulp mixture was then hydraulically pressed and the expressed liquid was vacuum-evaporated to 50º Brix. The residual peel was air-dried to less than 10% moisture.

All samples were analysed by the Harsy GC-MS method after storage for 1-4 months, except oil which was stored for as long as 9 months. Control samples of fruit and processed commodities were fortified and analysed concurrently with the treated samples. The recovery data are shown in Table 13 and the residues found in the treated oranges and their processed commodities in Table 14.

Table 13. Recovery of OPP and PHQ from fortified control oranges and processed products.

Sample	OPP added, mg/kg	OPP recovery, %	PHQ added, mg/kg	PHQ recovery, %
Whole orange	0.5	71, 71	0.2	67, 78
	1	86, 86	1	67, 82
	5	86, 82, 86, 82, 89, 89		
Juice	0.25	73	0.2	64, 70

Sample	OPP added, mg/kg	OPP recovery, %	PHQ added, mg/kg	PHQ recovery, %
	1	88, 75, 89	1	69, 67
	5	89, 83		
Dry pulp	0.05	90	-	
	0.5	89	-	
	1	100, 80	-	
	5	85, 90		
Oil	2	89, 96	1	44, 43
	5	79, 90	5	56, 52

Table 14. Concentrations of OPP and PHQ in oranges treated with a foaming cleaner (1.45%) and a storage wax (1.0%) and their processed products.

Sample	Day 0 residue, mg/kg	Day 28 residue, mg/kg	Day 56 residue, mg/kg	Day 0 processing factor	Day 28 processing factor	Day 56 processing factor
OPP						
Whole orange						
1	13.6, 13.4 (13.5)	8.90, 8.16 (8.53)	9.86, 10.1 (9.98)	-	-	-
2	18.4, 15.6 (17.0)	10.1, 13.5 (11.8)	7.85, 8.89 (8.37)	-	-	-
Juice						
1	0.263, 0.302 (0.283)	0.278, 0.320 (0.299)	0.344 0.325 (0.335)	0.021	0.035	0.034
2	0.314, 0.307 (0.311)	0.438, 0.426 (0.432)	0.324, 0.351 (0.338)	0.018	0.037	0.040
Dry pulp						
1	40.1, 38.5 (39.3)	38.7, 10.9 (24.8)	38.1, 36.3 (37.4)	3.0	2.9	3.7
2	39.2, 35.0 (37.1)	52.1, 52.2 (52.2)	45.9, 43.6 (44.8)	2.2	4.4	5.4
Oil						
1	1168, 1183 (1176)	866, 795 (831)	622, 693 (658)	88	97	66
2	1378, 1232 (1305)	933, 974 (954)	876, 877 (877)	77	81	105
PHQ						
Orange						
1	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	0.247, 0.225 (0.236)	-	-	-
2	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	-	-	
Juice						
1	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	~1	~1	~1
2	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	<0.2, <0.2 (<0.2)	~1	~1	~1

Sample	Day 0 residue, mg/kg	Day 28 residue, mg/kg	Day 56 residue, mg/kg	Day 0 processing factor	Day 28 processing factor	Day 56 processing factor
Oil						
1	<1.0, <1.0 (<1.)	<1.0, <1.0 (<1.0)	<1.0, <1.0 (<1.0)	-	-	-
2	<1.0, <1.0 (<1.0)	<1.0, <1.0 (<1.0)	<1.0, <1.0 (<1.0)	-	-	-

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Residues of OPP in fresh citrus fruits reported by citrus packing houses in the USA

Fresh citrus fruit treated with various formulations containing SOPP are often sampled at packing houses in the USA to check that the fruit has been treated according to label directions and that residues of OPP do not exceed the established US tolerance of 10 mg/kg. Reports of such monitoring by several US formulators of SOPP products were supplied.

The Brogdex Company provided residue data for 63 samples of Navel oranges, lemons and Valencia oranges treated with SOPP at 3 to 20 g/kg in 1998 (Appel, 1999). The residues ranged from 0.5 to 4.37 mg/kg, with an overall average of 2.24 mg/kg.

Elf Atochem North America provided extensive data on OPP residues in citrus fruit as determined in their laboratory from 1994 to 1998 (Wartanessian, 1999). All of the samples were of fruit that had been treated with OPP. Analyses were by method 415B. Residues of OPP in about 500 samples of grapefruit (mainly Florida) ranged from 0.1 to 2.5 mg/kg, with annual averages of 0.3 to 0.6 mg/kg; in about 330 samples of California lemons from 0.1 to 6.6 mg/kg, with annual averages of 0.8 to 1.6 mg/kg; in about 500 samples of Navel and Valencia oranges from California and Florida from 0.1 to 7.6 mg/kg, with annual averages of 0.4 to 0.9 mg/kg, and in 38 samples of (mainly Florida) tangerines from 0.1 to 0.8 mg/kg, with annual averages of 0.3 to 0.5 mg/kg.

FMC Food Tech, Citrus Systems, provided results of analyses in 1998 for OPP in >100 samples of grapefruit, lemons and Navel and Valencia oranges that had been treated with OPP (Nguyen, 1999). The residues ranged from 0.1 to 6.8 mg/kg in lemons. The highest residue found in 40 samples of oranges was 6.0 mg/kg.

Sunkist Growers reported residues of OPP found in 1996 and 1997 in about 1200 samples of Ruby Red and white grapefruit, Navel and Valencia oranges, lemons, tangerines, tangelos, mandarins, minneola, pummelo and oroblanco, grown in Arizona and California and treated in affiliated packing houses. The OPP residues ranged from 0.12 to 7.81 mg/kg, with the majority below 3 mg/kg (Mulligan, 1999). A large number of OPP residues were reported as “non-detected,” possibly because the fruit had been treated with fungicides other than OPP. The LOD was 0.10 mg/kg in the method used by Sunkist.

Data on residues of OPP in pears were not available from packing houses in the Pacific Northwest.

Residues of OPP in citrus fruit and pears reported by government laboratories

The US FDA has reported the results of a special pesticide residue monitoring study in which 4000 samples of infant foods and adult foods eaten by infants or children were analysed (Yess *et al*., 1993). Samples of fresh fruit were collected from markets in four geographic areas in the USA and analysed

as the whole, unwashed, unpeeled product. Residues of OPP were found in only 12 of 862 samples of oranges (1.4%), with a maximum of 4.4 mg/kg. No OPP was detected in the 571 samples of pears analysed in the study.

A later study by the US FDA focused on the incidence and level of pesticide residues in domestic and imported pears and tomatoes (Roy *et al*., 1995). One of the pesticides determined was OPP in a total of 710 domestic and 949 imported pear samples. About 95% of the fresh pears consumed in the USA are domestically grown, with about 97% of the production located in northwestern States (California, Oregon and Washington). Although Bartlett pears are grown on the largest area, only 30% of this early variety are sold as fresh fruit. Sampling was at a total of 227 domestic pear establishments, with 2.3 kg of pears taken from randomly selected cartons destined for retail markets. Analyses for residues of OPP were by HPLC with an acetone-water mobile phase and a fluorescence detector. The limit of determination was 0.10 mg/kg. All significant residues were determined with a second column and detector combination or by GC-MS to confirm the identity of the residues. Residues of OPP were found in 125 of 710 samples of domestic pears (18%) with a maximum of 2.6 mg/kg and in 28 of 949 samples of imported pears (3%) with a maximum of 2.2 mg/kg.

The Residue Branch of the USDA recently provided a summary and details of the incidence and level of OPP residues found in grapefruit, oranges, orange juice and pears analysed in 1992-1997 as part of the Pesticide Data Program (Fry, 1999). The samples were collected and analysed by participating State Laboratories in California, Florida, Michigan, North Carolina, New York, Ohio, Texas and Washington, using sensitive multiresidue screening methods (GLC with EC detection, GC-MS, HPLC with post-column derivatization and fluorescence detection). A total of 788 samples of grapefruit were analysed for OPP in 1992-1993 with 14 detections at levels between 0.015 and 0.055 mg/kg, 2116 samples of oranges during 1992-1996 with 283 between 0.010 and 3.6 mg/kg, 601 samples of orange juice in 1997 with 16 between 0.017 and 0.033 mg/kg, and 654 samples of pears in 1997 with 21 between 0.005 and 11 mg/kg.

Most of the OPP residues found in these commodities were <0.1 mg/kg, with 45 samples containing between 0.1 and 1 mg/kg and 32 samples containing >1 mg/kg. The highest residues were in pears collected in 1997, when post-harvest treatment with OPP increased because other fungicides such as benomyl were no longer available to control decay in stored pears.

The government of The Netherlands submitted data on residues of OPP in food in commerce in 1997 and in the period 1994-1996. In 1997, 30 of 177 citrus samples (17%) contained residues above 1 mg/kg, but below the MRL of 12 mg/kg. In 1994-1997, 254 of 665 citrus samples (38%) contained >1 mg/kg of OPP, three of them at or above the national MRL at 12-14 mg/kg.

NATIONAL MAXIMUM RESIDUE LIMITS

Leng (1999) compiled a Table of national MRLs for 2-phenylphenol and its sodium salt from information in the 1990 Canadian compendium. The governments of The Netherlands and Australia also reported their national MRLs.

Country	MRL, mg/kg	Commodities
Argentina	5	orange, grapefruit, lemon, lime, kumquat
Australia	25	pears
	20	carrots, peaches
	15	plums, prunes, sweet potatoes,
	10	melons (except watermelon), citrus fruit, cucumbers, peppers, pineapples, tomatoes
	3	cherries, nectarines
Austria	10	citrus fruit
Canada	25	Apples, pears, carrots, peaches, plums, sweet potatoes
	10	cantaloupes, citrus fruits, cucumbers, bell peppers, pineapples, tomatoes

Country	MRL, mg/kg	Commodities
Czechoslovakia	25	pears
	20	peaches
	15	plums, sweet potatoes
	10	gourds, citrus fruits, cucumbers, pineapples, tomatoes, green peppers
	3	nectarines, cherries
Denmark	5	citrus fruit (subsequently raised to 12 mg/kg?)
	0.1	others (cereal grains excluded)
Germany	10	citrus fruits
Hungary	25	apple, pear
	20	peach, carrot
	10	pineapple, melon, cucumber, tomato, black (?) pepper
	3	cherry, nectarine
Israel	15	plums
	10	citrus fruit, pineapple
Kenya	120	cantaloupes (whole)
	25	pears
	20	carrots, peaches
	15	sweet potatoes, apples, plums (including fresh prunes)
	10	citrus fruit, cucumbers, peppers, cantaloupes (edible portion), pineapples, tomatoes
Netherlands	12	citrus fruit, marmelades
	25	pome fruit
	20	peaches, carrots
	15	plums, sweet potatoes
	10	kiwifruit, pineapples, fruiting vegetables
	3	cherries, nectarines
	1	other food commodities
South Africa	10	citrus (for local use)
Spain	12	citrus fruit
	10	pears, apples, melons
	0.1	other plant products
Sweden	10	fruits and vegetables
Switzerland	10	citrus fruit (whole)
USA	125	cantaloupes (no more than 10 in edible portion)
	25	apples, pears
	20	carrots, peaches, plums (fresh prunes), kiwifruit
	15	sweet potatoes
	10	cantaloupes (edible portion), citrus fruits, cucumbers, peppers (bell), pineapples, tomatoes
	5	cherries, nectarines

APPRAISAL

The 1969 JMPR recommended MRLs for 2-phenylphenol (OPP) and its sodium salt (SOPP) in several fruits. 2-Phenylphenol was originally scheduled for periodic re-evaluation of residues by the 1994 JMPR, but was withdrawn because the manufacturer indicated that it was not supporting the existing CXLs and the data base was considered insufficient to support a periodic review. OPP was rescheduled for periodic re-evaluation of residues by the 1999 JMPR (ALINORM 95/24A, Appendix IV). The California Citrus Quality Council (CCQC) and the Pear Bureau Northwest provided information in support of the periodic review. Additional information was supplied by the governments of Australia and The Netherlands.

Animal metabolism

Two lactating Nubian goats 2 to 4 years of age were dosed orally by capsule with [^{14}C]2-phenylphenol, labelled in the phenoxy ring daily for 5 consecutive days at an average dose level of 13.7 and 53.3 mg/kg b w/day. The doses were equivalent to 11.3 ppm and 32.1 ppm of the test

material in the diet, based on actual feed consumption during the test period. Milk, urine and faeces were collected daily from each animal. The goats were slaughtered about 23 hours after the last dose.

All samples were radioanalysed. In both goats >90% of the administered radioactivity was eliminated, mainly in the urine. The radioactivity in the milk reached a plateau on day 1 or 2 for both animals at 0.03% of the administered dose, 0.008 µg OPP equivalents/g from the low dose and 0.043 µg/g from the high dose. Radioactive residues from the low dose were ≤0.005 mg/kg in the fat, kidney, liver and muscle, and from the high dose 0.003 mg/kg in the fat, 0.020 mg/kg in kidney, 0.014 mg/kg in liver and <0.001 mg/kg in muscle.

The extracts of kidneys and liver were analysed by HPLC. The organic solvent extracts of milk was not analysed because of the very low levels of radioactivity. Reference standards included phenyl-1,4-benzoquinone (PBQ), OPP and phenylhydroquinone (PHQ). No peak corresponded to a reference standard in any extract. The largest single component detected was 0.007 mg/kg as OPD in the acetonitrile extract of kidney. In general, no other component accounted for more than 0.002 mg/kg. Extracts were not hydrolysed to release possible conjugates because of the low radioactivity.

The metabolism of OPP in rats, mice and humans was summarized without supporting details. Metabolism studies have shown that OPP is well absorbed and rapidly excreted in the urine. The main metabolite excreted by rats was OPP sulfate with lesser amounts of glucuronide conjugates of OPP and its hydroxylated metabolite phenylhydroquinone (PHQ). Trace amounts of phenyl-1,4-benzoquinone (PBQ) were also detected in urine These metabolites were also found in the urine of mice given 5 daily doses of OPP at 25 and 1000 mg/kg bw and in human male volunteers given a dermal application of [^{14}C]OPP at 0.006 mg/kg bw. The sulfate conjugate of 2,4'-dihydroxybiphenyl (DHB) was also identified. Little or no free OPP and no free PHQ or PBQ was found in mice, rats and humans.

The Meeting concluded that the metabolism of OPP in ruminants is adequately understood. OPP and/or its metabolites are eliminated in the urine and do not accumulate in any tissues or milk. OPP, PBQ and PHQ were not found in milk or tissues. Studies with rats and mice indicate that OPP is converted directly to the glucuronide and sulfate conjugates, and via a postulated 2,4'-DHB to a sulfate and via a postulated PHQ to PHQ glucuronide and sulfate.

Plant metabolism

The metabolism of OPP applied post-harvest to oranges and pears was reported. Oranges were dipped in either a 0.1% or 0.5% solution of radiolabelled OPP and were then stored for intervals from 2 hours–12 weeks under commercial storage conditions for pears at 1–4°C. Upon removal from storage, the oranges were rinsed with methanol to remove surface residues and then peeled. Pulp containing 6.2 mg/kg as OPP and juice 7.0 mg/kg as OPP from the 0.5% treatment after 12 weeks were extracted and analysed by HPLC. Peels taken at intervals were subjected to sequential extraction and enzyme, acid, and base hydrolysis.

The calculated total radioactive residue on whole oranges was 9–12 mg/kg from the 0.1% dip and 16 mg/kg from the 0.5% dip. Most of the radiolabelled residue (>95% of the TRR) remained in the rinse or the peel at all intervals. The main compound in the juice and pulp samples was OPP, 75% of the radioactivity in the pulp extract (0.14% of the TRR, 0.01 mg/kg) and about 51% of that in the juice extract (0.12% of the TRR, 0.01 mg/kg). Orange peel contained OPP and OPP conjugates (89% of the TRR) and phenylhydroquinone (3.6%).

Bosc pears were treated with an aqueous dipping solution of 40 g/kg unlabelled and (U-*phenoxy*-^{14}C]OPP. The pears were rinsed after treatment and stored at 1-4°C and 90% humidity for various periods (2 h–28 weeks). Pears taken from storage were rinsed with methanol to remove surface residues and peeled. Peels and pulp were extracted separately. Extracts were analysed by HPLC and GC-MS and LC-MS were used for qualitative identifications.

The pears sampled 28 weeks after treatment contained 42.2 mg/kg OPP equivalents. About 66% of the TRR was in the peel and 26% in the pulp. About 57% of the TRR in the peel and 23% in the pulp was identified as OPP and OPP conjugates, one a glucose conjugate. The rinse contained 4% of the TRR

The Meeting concluded that the metabolism of OPP in plants is adequately understood. Most of the residue in oranges and pears is OPP and OPP conjugates. PHQ (4% of the TRR) was found in orange peel. OPP did not translocate beyond the peel of oranges, but migrated substantially into the pulp of pears.

Environmental fate

Information was presented on the biodegradation of OPP in river water, activated sludge and municipal waste-water with a microbial inoculum (OECD Method 301B). In river water radiolabelled OPP at concentrations ranging from 1.2 to 120 µg/l was degraded to about 50% of the initial concentration in one week. The addition of $HgCl_2$ to inhibit biological activity reduced the decrease to only 10% after 30 days. In activated sludge, radiolabelled OPP at 9.6 mg/l was degraded to 50% of the initial concentration in 24 hours. OPP meets the criteria to be classed as readily biodegradable. Mineralization to $^{14}CO_2$ accounted for about 66% of the radioactivity after 11 days. In $HgCl_2$-treated controls <1% of the radioactivity was evolved as $^{14}CO_2$.

The Meeting concluded that OPP is readily degraded in surface waters and municipal waste mixtures and that the degradation is biologically mediated. The Meeting also concluded that information on the fate in soil is not required because OPP is used only as a post-harvest treatment in packing houses and similar indoor structures. Contamination of the soil is highly unlikely.

Analytical methods

Numerous methods exist for the determination of 2-phenoxyphenol and sodium 2-phenylphenate in crops. No methods are available for livestock commodities. The official enforcement method in the USA is a photometric method with an estimated limit of detection of 3 mg/kg. The chopped sample is steam distilled in aqueous phosphoric acid, the distillate is derivatized, and the absorbance at 500 nm is measured. Many laboratories now measure absorption after HPLC. With this variation the limit of determination is about 0.025 mg/kg.

Several HPLC methods that do not require distillation are described in the literature. One such method is routinely applied to citrus fruit by a major US citrus grower. A composite fruit sample is slurried and extracted with ethyl acetate. The extract is analysed by HPLC with fluorescence detection. The limit of detection is estimated to be 0.05 mg/kg OPP.

A GLC method is used industrially to measure residues in citrus fruit, kiwifruit and cantaloupes. Elf Atochem Method 415B involves reflux distillation with HCl and hexane. The distillate is extracted and analysed by GLC with a flame ionization detector and a capillary column. The limit of determination is 0.1 mg/kg.

The method used for trials and a processing study and proposed for enforcement in the USA is a GC-MS procedure. The blended fruit sample is simultaneously acid-hydrolysed, steam distilled and extracted in a micro-Nielson-Kryger apparatus. The extract is derivatized with BSTFA. The resulting trimethylsilyl ether is analysed by GC-MS in the selected ion mode. Ions monitored for OPP were 227, 242, 170 and 141, with m/z 227 used for quantification ion. The method can be adapted to determine PHQ. The limit of determination for OPP was 0.05 mg/kg in all citrus products except oil, in which it was 1 mg/kg.

The Meeting concluded that adequate methods exist for data collection and for MRL enforcement for OPP in fruit and fruit products.

Stability of residues in stored analytical samples

In storage stability studies on citrus OPP was stable at freezer temperatures in grapefruit for 6 months, lemons for 8 months, oranges for 7 months, orange juice for 5 months and orange oil for 9 months. PHQ was stable in grapefruit for 5 months and orange juice for 5 months, but unstable in oranges and orange oil. The PHQ data for lemons could not be interpreted.

A storage stability study on pears was conducted concurrently with the residue trials. OPP was stable in pears stored frozen for about 4 months.

The Meeting concluded that adequate storage stability data had been presented for OPP in citrus and processed citrus commodities and in pears.

Definition of the residue

In studies of metabolism in oranges and pears OPP and its conjugates constituted 90% of the total radioactive residue (TRR) in oranges and 87% of the TRR in pears. PHQ was found in orange peel at low concentrations (<4% of the TRR). It is therefore appropriate to define the residue for both enforcement and for the estimation of dietary exposure as the sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol. This applies to plant commodities only.

Residues resulting from supervised trials

Citrus fruits. US GAP encompasses only post-harvest fruit treatments. The trials complied with a foamer cleaning with brushes and spray for 10–60 sec at 1.45 kg sodium *o*-phenylphenate (SOPP) per hl or a waxing with brushes and spray at 0.97 kg SOPP per hl, with an application rate of the final mixture at 0.83 ml/kg fruit (1 gal/10,000 lbs.). Additional GAP not covered by the trials specifies (1) a dip/wash for 2–5 minutes with 0.36 kg SOPP per hl, followed by a fresh water rinse; and (2) a bin drench at 0.87 g SOPP per hl, with no rinse. The foamer cleaning would give the highest exposure to OPP.

Supervised trials were reported on lemons, oranges and grapefruits, two each on lemons and oranges in California, two on California grapefruit and two on Florida grapefruit. In each trial the fruit were subjected to a foamer cleaning with brushes using 1.45% anhydrous SOPP with a 30-second exposure. This was followed by the application of shipping wax containing 1.0% anhydrous SOPP, at 1 l of wax solution per 1200 kg of fruit, corresponding to maximum GAP; only one application of OPP is usually made. Some control samples contained OPP above the limit of determination (0.05 mg/kg), the range being <0.05–0.08 mg/kg. The concentration in the controls was at most about 2% of that in the treated samples and was not considered significant.

The residues in the whole fruit in rank order were 2.4 (3), 2.7, 5.2. 5.4, 6.5 and 6.7 mg/kg. The median is 3.95 mg/kg. The pulp samples were not analysed separately from peel, but the study of orange metabolism indicated that no more than 5% of the radioactive residue was likely to be found in the pulp. The STMR for pulp may be estimated as 0.05 x 3.93 mg/kg, and 0.20 mg/kg.

The number of trials is inadequate for any individual commodity, but 8 trials are acceptable for the citrus group. The Meeting estimated an STMR of 3.9 mg/kg and a maximum residue level of 10 mg/kg, confirming the existing MRL for citrus fruits.

Pears. US GAP specifies the post-harvest treatment of pears as (1) foamer and spray cleaning with 1.3 kg SOPP/hl for 15–30 seconds followed by a rinse, or (2) dipping in 0.35 kg SOPP/hl solution for 1.5–4 minutes, followed by a rinse.

In two trials in the USA, pears were dipped in a 0.49% solution of SOPP for 2 minutes, followed by a water rinse. The trials were according to maximum GAP and the residues were highest on the day of treatment. The residues were 0.82 and 1.4 mg/kg.

The Meeting could not estimate an STMR or maximum residue level as there were only two trials, and recommended the withdrawal of the existing MRL.

Apples. No trials were reported. The Meeting recommended the withdrawal of the existing MRL.

Animal feeding studies

No studies were reported. Orange pulp is used in cattle feed. The ruminant metabolism study showed no detectable residues of OPP or PHQ. Conjugates were not determined. The high-dose rate, equivalent to 32 ppm in the feed, represents approximately 6 times the theoretical maximum intake of OPP by cattle. This is based on the highest residue found in citrus trials according to GAP, 6.7 mg/kg, the average processing factor for converting citrus to dried pulp, 3.6 and the percentage of citrus pulp in the diet, 20%, and 6.7 mg/kg x 3.6 x 0.2 = 4.8 ppm. At the sixfold rate, more than 90% of the residue was eliminated. There was no propensity for the residue to accumulate in fat and muscle. Low levels of residues were found in the milk (0.04 mg/kg), kidney (0.02 mg/kg) and liver (0.01 mg/kg). These residues consisted of multiple components, none of which exceeded 0.007 mg/kg. Neither OPP nor PHQ was found. Measurable residues from the ingestion of OPP would not be expected from current treatments according to GAP. This assumes that additional bioaccumulation does not occur with exposure periods greater than 5 days.

The Meeting concluded that maximum residue levels need not be estimated for animal commodities.

Processing

Studies of the conversion of treated oranges into orange juice, orange oil and dried pulp were reported. Oranges were treated by a foamer cleaning with a 14.5 g/kg solution of SOPP for 120 seconds, followed by application of shipping wax containing 10 g SOPP per kg. The oranges were scarified before treatment to increase the uptake of OPP. The treatments represented maximum GAP, but the scarification would be expected to produce higher residues. Oranges were processed on the day of treatment and 28 and 56 days later. Two independent trials were conducted on each day, giving a total of six trials.

The residues decreased in converting oranges to juice. The processing factors were 0.018, 0.021, 0.034, 0.035, 0.037 and 0.040, an average processing factor of 0.031. The Meeting estimated an STMR for orange juice of 0.12 mg/kg, based on the STMR for citrus of 3.9 mg/kg and the average processing factor. The Meeting also estimated a maximum residue level for orange juice of 0.5 mg/kg, based on the maximum residue level for citrus of 10 mg/kg and the maximum processing factor of 0.040.

The residues increased in orange oil. The processing factors were 66, 77, 81, 88, 97 and 105, an average of 86. The Meeting estimated an STMR for orange oil of 340 mg/kg from the STMR for

citrus of 3.9 mg/kg and the average processing factor, and a maximum residue level of 1000 mg/kg from the maximum residue level for citrus of 10 mg/kg and the maximum processing factor of 105.

The residues were increased slightly in dried pulp, an animal feed item. The processing factors were 2.2, 2.9, 3.0, 3.7, 4.4 and 5.4. The Meeting estimated a maximum residue level for dried orange pulp of 60 mg/kg, based on the citrus maximum residue level and the maximum processing factor, 10 x 5.4 = 54 mg/kg.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLS.

Definition of the residue for plant commodities, for compliance with MRLs and for the estimation of dietary intake: sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FP 0226	Apple	W	25 Po	-
FC 0001	Citrus fruits	10	10 Po	0.20
AB 0001	Citrus pulp, dried	60	-	-
JF 0004	Orange juice	0.5	-	0.12
-	Orange oil		-	340
FP 0230	Pear	W	25 Po	-

FURTHER WORK OR INFORMATION

Desirable

A ruminant feeding study at the level of the estimated dietary intake based on citrus pulp consumption and at 10 and 100 times that level. Milk and tissues should be analysed for OPP and PHQ, free and conjugated.

DIETARY RISK ASSESSMENT

Chronic intake

STMRs for one raw commodity and one processed commodity were used for a chronic dietary intake assessment. The International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on these STMRs, were all 0% of the ADI. The Meeting concluded that the intake of residues of 2-phenylphenol resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The Meeting concluded that an acute RfD for 2-phenylphenol is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard, and residues are therefore unlikely to present an acute risk to consumers.

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PHOSALONE

EXPLANATION

Phosalone, a phosphorodithioate acaricide and insecticide, was re-evaluated by the 1994 JMPR in the CCPR Periodic Review Programme. That Meeting concluded that the existing CXLs for phosalone should be withdrawn, owing to inadequacies in the available information on storage stability and the effects of processing. The 1996 CCPR was informed that new residue data on apples, citrus fruits, grapes and potatoes would become available in 1999, and decided to maintain the CXLs for these commodities for four years pending the evaluation by the 1999 JMPR. The 1999 CCPR recommended withdrawal of the CXLs for citrus fruits, grapes and potato, however, as they were no longer supported. The toxicology was reviewed at the 1997 JMPR which allocated an ADI of 0.02 mg/kg bw.

The Meeting received new or revised information on physical and chemical properties, metabolic and environmental fate, analytical methods, stability of analytical samples, use patterns, supervised trials, effect of processing apples, and national MRLs.

Physical and chemical properties

The Meeting received the revised information on physical and chemical properties shown below.

Pure active ingredient

Octanol/water partition coefficient:	log P_{ow} = 4.01 at 20°C (Cousin, 1995)
Solubility:	in water 1.4 mg/l at 20°C (Cousin, 1997a)
Photolysis:	in water at pH 5, decomposition is very rapid (half-life 15-20 min) (Laurent *et al.*, 1977). The quantum yield (Φ_{300}) at 300 nm for phosalone in aqueous solution was determined to be 0.19 (Boinay, 1994).

Technical material

Purity:	930 g/kg (minimum)
Melting range:	42 to 48°C
Specific gravity:	1.338 g/ml at 20°C (Pollard, 1987)
Vapour pressure:	4.57 x 10^{-7} mn Hg at 25°C (Hoffman, 1989)
Solubility:	in organic solvents at 20°C: (Cousin, 1997a) acetone >1000 g/l dichloromethane >1000 g/l ethyl acetate >1000 g/l n-heptane 26.3 g/l toluene >1000 g/l methanol >1000 g/l

n-octanol 266.8 g/l

Stability: Not highly flammable, not autoflammable, not explosive (Fillion, 1997), does not have oxidizing potential (Cousin, 1997b)

Formulations Emulsifiable concentrate, wettable powder, flowable

METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

The Meeting received studies on apples (Kimmel *et al*., 1990) and grapes (Periasamy *et al*., 1995).

Apples. Apple trees were brushed with [*phenyl*-^{14}C]phosalone on the surface of individual leaves and fruits at a rate equivalent to 3.3 - 3.5 kg ai/ha, grossly in excess of the recommended application rate. Single applications were made at different times to each of two trees. On the first tree the chemical was applied to all immature fruits (3.8 cm diameter) and to leaves on 3 selected branches, and samples were taken 14 days after application. On the second the compound was applied to all fruits (6.5-7.5 cm diameter; about 4 weeks before maturity) and leaves on three selected branches and samples were taken 14 days and 24 days after application. Only the final samples were analysed because the later harvest would be likely to identify more extensive metabolism. Apples and leaves were rinsed, and extracted with methanol. The extractable residues were characterized by TLC and HPLC.

In the leaves, 57% of the total radioactive residue (TRR) was contained in the rinse fractions with 43% in the homogenized leaf (Table 1). In contrast, the apple fruits showed <1% of the radioactivity in the rinse fraction, 1-2% in the pulp, and 97-98% in the peel.

Table 1. Total radioactive residues in apple leaves and fruits.

Treatment	Sample		^{14}C, mg/kg as phosalone	% of TRR
Application to immature fruit (Treatment I)	Leaf	Rinse	511	57
		Leaf homogenate	389	43
		TRR	**900**	**100**
	Fruit	Rinse	0.21	0.26
		Peel	80	99
		Pulp	0.63	0.78
		TRR	**80.84**	**100.04**
Application to near mature fruit (Treatment II)	Leaf	Rinse	453	59
		Leaf homogenate	318	41
		TRR	**771**	**100**
	Fruit	Rinse	0.16	0.27
		Peel	58	98
		Pulp	0.87	1.5
		TRR	**59.03**	**99.77**

Table 2 shows the efficiency of the methanol extraction.

Table 2. Recovery of [^{14}C]phosalone from apples.

Sample	Treatment I	Treatment II

	Methanol extractable, %[1]	Unextractable, %[1]	Methanol extractable, %	Unextractable, %
Apple leaf	99	3.4	92	8.4
Apple peel	90	8.2	89	3.2
Apple pulp	73	NA[2]	104	4.9

[1] Based on total dpm determined by combustion of sample before extraction
[2] Not analysed

Phosalone was only metabolized to a limited extent. Residues were quantitatively extracted and phosalone accounted for 75-92%. Phosalone oxon and 6-chlorobenzoxazolone were found at low levels (2-7%) in leaf extracts and rinses (Table 3).

Table 3. Distribution and identity of residues in apples following application of [^{14}C]phosalone.

Sample	Treatment I		Treatment II	
	% of TRR	mg/kg as phosalone	% of TRR	mg/kg as phosalone
Leaf rinse	100	511	100	453
Phosalone	86	441	83	376
Phosalone oxon	3.5	18	2.2	10
6-chlorobenzoxazolone	4.5	23	6.4	29
Unknowns	3.7	19	5.1	23
Polar products	2.2	11	3.3	15
Leaf extract	100	376	100	291
Phosalone	88	329	75	219
Phosalone oxon & 6-chlorobenzoxazolone	6.9	26	5.6	16
Polar products	5.6	21	19	56
Peel extract	100	73.1	100	55.8
Phosalone	92	67	88	49
Unknowns	2.3	1.7	3.9	2.2
Polar products	6.0	4.4	8.2	4.6
Pulp extract	not analysed		101	0.83
Phosalone			51	0.42
Unknowns			17	0.14
Polar products			33	0.27

Grapes. Grape bunches on two vines were treated with phenyl-labelled [^{14}C]phosalone at the equivalent rate of 2.1 kg ai/ha, either as a single application 23 days before harvest or as two applications each at 1.05 kg ai/ha 23 and 9 days before harvest. This was highly atypical practice, resulting in exaggerated application. The spray was directed on the bunches of grapes, with foliage held away from the bunches. After harvest, grapes were rinsed and separated into juice and pulp, which were analysed. Samples were characterized by TLC and HPLC. Polar fractions in the juice and pulp were analysed by derivatization and chemical and enzymatic hydrolysis. The limit of detection for combustion radioassay and for HPLC analysis of the solvent-extractable residues was <0.01 mg/kg.

Most of the radioactivity was found in the pulp with very low amounts in the rinse or juice There was no difference in distribution between the two application schemes (Table 4).

Table 4. [^{14}C]phosalone residues in grapes.

Sample	1 application		2 applications	
	mg/kg as phosalone	% of TRR	mg/kg as phosalone	% of TRR
Rinse	0.51	1.8	0.45	1.6

Juice	0.87	3.1	0.70	2.6
Pulp	26	95	26	96

The results of the analysis of the rinses, juice and pulp are shown in Table 5. The parent phosalone was the major residue in each fraction. Examination of the more polar group of metabolites in the juice and pulp samples by chemical and enzymatic hydrolysis indicated that the metabolites were mainly glycosides.

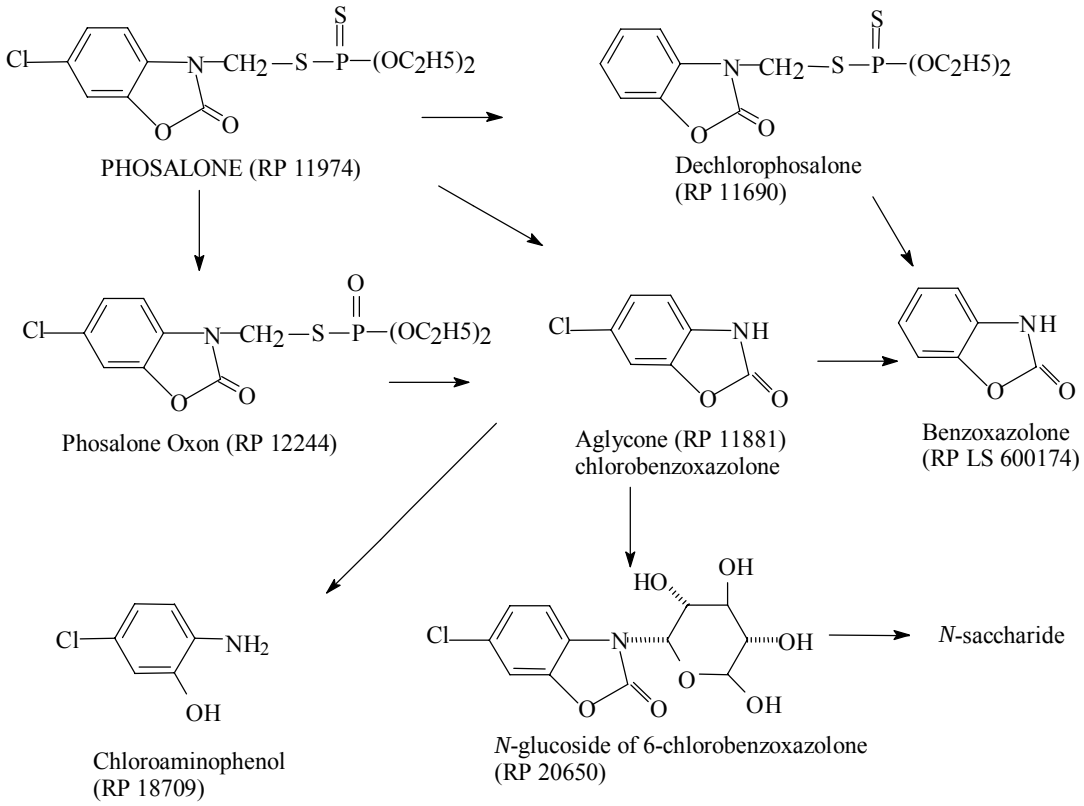
Table 5. Distribution of [^{14}C]phosalone and its metabolites in grapes.

Compound	Rinse		Juice		Pulp		Total	
	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR
1 Application								
Phosalone	0.18	0.65	0.39	1.4	24	86	24.6	88
Phosalone oxon	0.14	0.5	0.016	0.06	0.19	0.68	0.35	1.3
Benzoxazolone			0.019	0.07	0.01	0.04	0.029	0.1
6- chlorobenzoxazolone	0.007	0.03	0.005	0.02	0.008	0.03	0.02	0.07
2-amino-5-chlorophenol					0.027	0.1	0.027	0.1
Dechloro-phosalone					0.055	0.2	0.055	0.2
N-glucoside of chlorobenzoxazolone			0.057	0.21	0.036	0.13	0.093	0.33
N-saccharide of chlorobenzoxazolone			0.17	0.61	0.031	0.11	0.2	0.72
Unknowns A-1			0.061	0.22	0.013	0.05	0.074	0.27
Unknowns A-2					0.048	0.17	0.048	0.17
2 Applications								
Phosalone	0.06	0.22	0.33	1.2	27	100	27.4	102
Phosalone oxon	0.17	0.63	0.034	0.13	0.34	1.3	0.54	2.02
Benzoxazolone	0.005	0.02	0.033	0.12			0.038	0.14
6- chlorobenzoxazolone	0.009	0.03			0.049	0.18	0.058	0.22
2-amino-5-chlorophenol					0.019	0.07	0.019	0.07
Dechloro-phosalone					0.028	0.10	0.028	0.10
N-glucoside of chlorobenzoxazolone			0.049	0.18	0.024	0.09	0.073	0.27
N-saccharide of chlorobenzoxazolone			0.08	0.30	0.02	0.07	0.100	0.37
Unknowns A-1			0.029	0.11	0.008	0.03	0.037	0.14
Unknowns A-2					0.032	0.12	0.032	0.12

[1]As phosalone

The metabolism of phosalone in grapes involves dechlorination, oxidation, hydrolysis and conjugation. Several potential metabolites were specifically looked for but not found. These included phenoxazone, 6-chloro-3-mercaptomethylbenzoxazolone, 6-chloro-3-methylsulfinylmethylbenzoxa - zolone, 6-chloro-3-methylthiomethylbenzoxazolone, 6-chloro-3-methylsulfonylmethylbenzoxa- zolone, and other dephosphorylated derivatives of chlorobenzoxazolone.

Figure 1. Proposed metabolic pathways of phosalone in plants.



Environmental fate in soil, water and air

Photolysis in water

Laurent *et al*. (1977) studied the photodegradation of phosalone at a concentration of 1 mg/l in water buffered at pH 5 at 25°C. Phosalone is most stable to hydrolysis at pH 5 (less than 10% degradation after one month). The light source was a mercury vapour arc, with wavelengths below 290 nm filtered out. The power in the UV band (290-400nm) was about 9 W. Degradation kinetics were examined in both distilled water and water buffered to pH 5 using technical phosalone (not radiolabelled), with levels determined by GLC with an ECD. Phosalone was found to decompose very rapidly, with a half-life of 15-20 minutes in both distilled water and the buffered solution. The addition of acetone (2%) reduced the degradation rate by a factor of 1.5 to 2 but also changed the quantity and nature of the degradation products.

Photolytic degradation products were determined using [^{14}C]phosalone in buffered solution (pH 5) without acetone. Samples were irradiated for times estimated to result in 25%, 50% and 75% degradation. The irradiated solutions were extracted with dichloromethane and ethyl acetate. The overall recovery was >96%. In the solution with 75% degradation (confirmed by GLC analysis) 0.25% of the radioactivity was recovered in the traps for volatiles and 4.4% from the residual aqueous phase.The organic extract contained 92.2% of the applied radioactivity as phosalone, hydroxy-phosalone, and about 20 other degradation products none of which exceeded 5% (0.05 mg/kg as phosalone equivalents). Analyses were by TLC in various systems with liquid scintillation counting (LSC) and confirmation of identities by IR, MS and NMR.

Samples in buffer solution with acetone were irradiated for times estimated to result in 25%, 40% and 68% degradation. The overall recovery was >85%. In the solution with 68% degradation (confirmed by GLC) 14.5% of the radioactivity was recovered in the volatile traps and 20.7% from the residual aqueous phase. The minor products hydroxy-phosalone, phosalone oxon and 6-

chlorobenzoxazolone were found in the organic extract, which contained 50.5% of the applied radioactivity.

Boinay (1994) reported the quantum yield at 300 nm of the direct photolysis of phosalone in aqueous solution, determined with an actinometer. The concentration of the test solution was 5.21 mg/l (1.409 x 10^{-5} mol/l). The Δn and Na values were calculated to be 2.751 x 10^{-9} mol/sec and 2.08 x 10^{-8} Einstein/l/sec for irradiation for 0-0.5 h in the first assay, giving a calculated quantum yield of 0.13. In the second assay, Δn and Na were calculated to be 2.273 x 10^{-9} mol/sec and 9.185 x 10^{-9} Einstein/l/sec and the quantum yield (Φ_{300}) was 0.25, giving a mean value of 0.19.

Maestracci (1995) calculated the environmental photolytic half-life of phosalone in a natural aquatic system. The molar extinction coefficient in the range 292.5-800 nm was determined by Jendrzejczac (1994). The half-life of phosalone in a natural aquatic system in Europe (52° north latitude) was calculated to range from 49 hours in July to 1354 hours in December.

Photolysis in air

Maestracci (1994) estimated the rate of photochemical transformation of phosalone in the troposphere, the main reaction being between hydroxy radicals and the phosphorus-containing group. The estimated reaction constant at 298°K was 9.34 x 10^{-3} s^{-1} which corresponds to a half-life of about 74 daylight seconds.

Biodegradability

Muttzall and Hanstveit (1989) reported the inherent biodegradability of phosalone which was determined in the modified Sturm test (OECD-TG 301B, 1981) during a six-week period in an activated sludge taken from an oxidation ditch. Because of the low water solubility of phosalone, [^{14}C]phosalone, applied at concentrations of 1 and 2 mg/l, was used in addition to unlabelled phosalone in order to measure the degradation adequately. Radioactivity in the CO_2 traps was determined at 1, 2, 3, 4, and 6 weeks. About 20% of the initial radioactivity were detected as $^{14}CO_2$ at the end of the sixth week.

Aerobic degradation in soil

Skinner and Jao (1995) reported the aerobic degradation of [^{14}C]phosalone in German standard soil 2.2 (a loamy sand, pH 5.6, 0.62% organic matter). Phosalone was applied at an initial concentration of 1 μg/g soil (equivalent to 1 kg ai/ha) and samples were maintained in the dark at 20 ± 2°C at 40% of maximum water holding capacity for up to 45 days. The overall recovery of ^{14}C was 99.8 ± 2.9%. Phosalone was degraded rapidly with a half-life of 2.9 days. Production of $^{14}CO_2$ continued throughout the sampling and CO_2 was the most abundant single product, representing 4% of the dose. The total of all degradation products in the extract accounted for 5.0% of the applied dose. Phenoxazone was observed only in day 30 and day 45 extracts and represented ≤ 0.7% of the applied dose, but its presence indicates the transient existence of its precursors in the degradation pathway. Some minor products, 6-chlorobenzoxazole, 2-amino-5-chlorophenol and phosalone oxon, were detected, all representing ≤2% of the applied dose. Unextracted radiocarbon increased to an average of 84.7% by day 30, then decreased to 80.6% at 45 days. Bound residues were characterized; none of the individual components in the fulvic acid, hymatomelanic acid, or humin fractions accounted for more than 10% of the applied dose.

The rate of aerobic degradation of [^{14}C]phosalone was investigated at an initial concentration of 1 mg/kg (1 kg ai/ha) in four soils from Germany, one of which was used to establish the degradation pathways in aerobic soil. Soil samples were maintained in the dark at 20 ± 2°C and at 40% of maximum water holding capacity Incubation was continued until two consecutive samplings showed that less than 10% of the applied phosalone remained intact, which was between 42 and 45

days. All samples were assayed by LSC, extracted, and the residues characterized and quantified by TLC and HPLC. Phosalone was found to be degraded rapidly in all four soils (Table 6).

Table 6. Degradation rates of phosalone in four soils under aerobic conditions.

	DT-50 (days)	DT-90 (days)
Standard Soil 2.1	4.1	16.5
Standard Soil 2.2	2.9	30
Standard Soil 2.3	0.8	19.2
German Field Soil	0.8	13.3

At the final sampling the largest single component in the combined initial extracts in any of the soils accounted for 4.7% of the applied dose (on day 28 in Standard Soil 2.1). Phenoxazone was detected by HPLC in all three soils but did not exceed 1.5% of the applied dose. Radioactivity from the three precursors of phenoxazone represented a total of ≤2.0%. CO_2 accounted for 3.5 to 5.9% of the applied dose at the end of the study. The unextractable radiocarbon increased over time, rising to between 74.4 and 84.6% of the applied dose. No organic volatiles were found at any time (Table 7).

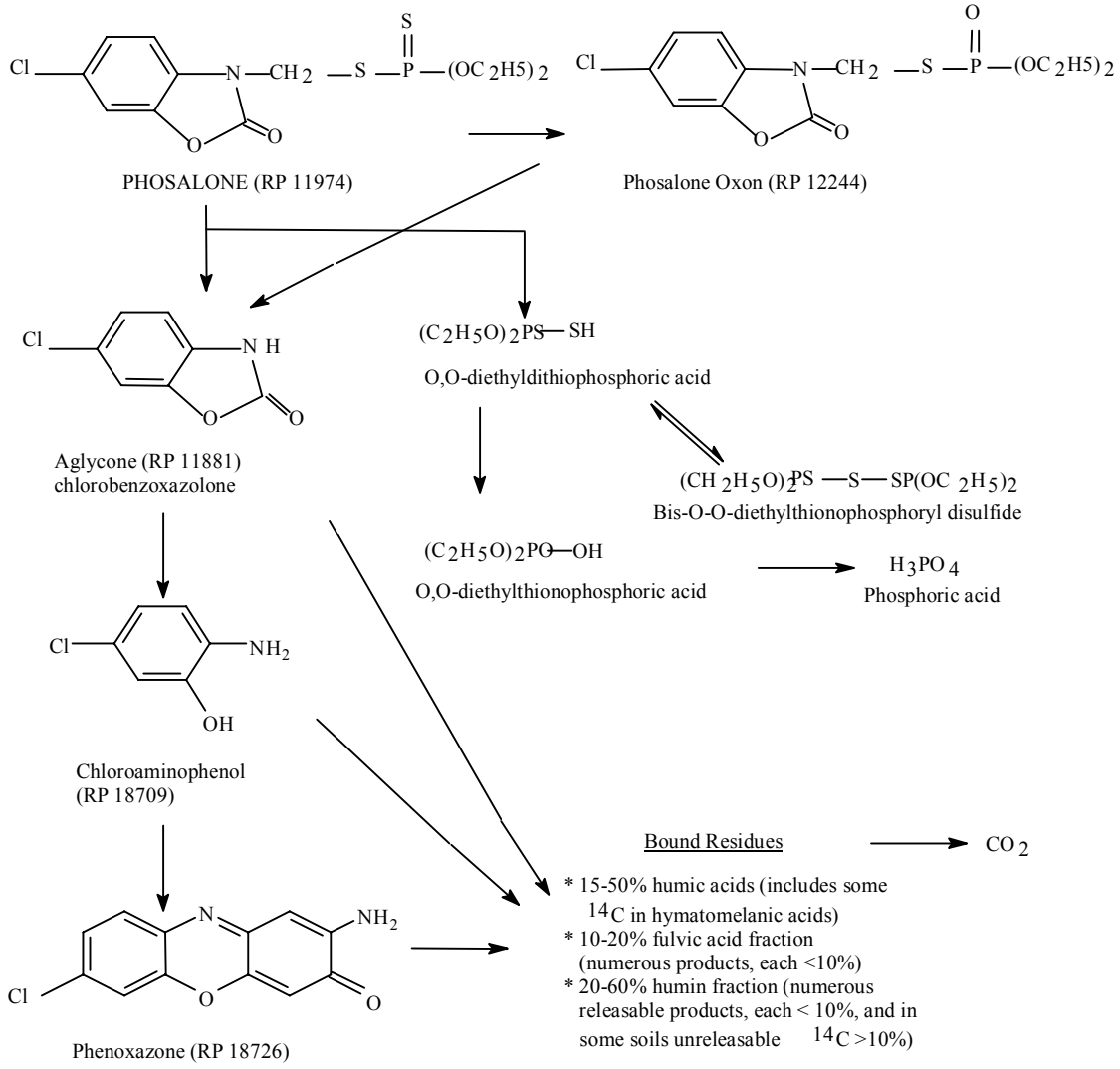
Table 7. Distribution of radioactivity in soil after 45 days.

	% of applied dose					
Soil	Phosalone	Other extracted	Unextracted	$^{14}CO_2$	Other volatiles	Total recovery
Speyer 2.1	4.3	14.8	74.4	3.5	0.0	97.0
Speyer 2.2	7.4	5.0	80.6	4.0	0.0	96.9
Speyer 2.3	5.6	7.8	76.0	4.8	0.0	94.2
Sandy Loam	4.5	3.9	84.6	5.9	0.0	98.9

Unextracted soil residues from the last sampling were characterized. The results were similar to those reported in the degradation study with no single component accounting for more than 10% of the applied ^{14}C.

Proposed degradation pathways are shown in Figure 2.

Figure 2. Proposed degradation pathways of phosalone in soil under aerobic conditions.



Anaerobic degradation in soil

Clarke (1999) reported the anaerobic degradation of [1-*phenyl*-^{14}C]phosalone in sandy loam soil (ADAS and USDA classifications) incubated at 20°C in the dark.

Soil was flooded and purged with nitrogen for 39 days before treatment to establish anaerobic conditions. Phosalone was applied to the water surface at a rate equivalent to 1.04 kg ai/ha and samples were incubated for up to 77 days. Additional flasks were treated with [^{14}C]phosalone at a rate equivalent to 1.0 kg ai/ha after 97 days incubation under anaerobic conditions to confirm the rates of degradation in the water phase and transfer to the soil phase, which were found to be extremely rapid in the early samples. Radioactivity was rapidly transferred to the soil, with only 14% of the applied ^{14}C remaining in the water after 7 days, and 2% after 77 days. Degradation products were identified by HPLC co-chromatography with certified reference standards and identities were confirmed, where possible, by mass spectral analysis. Overall recoveries ranged from 90 to 100%. In the water phase, phosalone was rapidly degraded to 2-amino-5-chlorophenol (chloroaminophenol), which reached a maximum of 20% of the applied radioactivity after 3 days and then decreased. Low levels of 6-chloro-3*H*-benzoxazol-2-one, the precursor of chloroaminophenol, were detected up to 3 days at 0.5-3.5% of the applied radioactivity. In the soil phase, phosalone was rapidly degraded to chloroaminophenol, which reached a maximum of 8% of the applied radioactivity at day 14, and 6-chlorobenzoxazolone

which reached a maximum of 2% at day 56. No significant levels of volatile compounds were found (<0.5% of the applied ^{14}C after 77 days). Seven-day samples containing residues which were not extracted by solvents were subjected to further treatment to determine whether any additional radioactivity could be released. Ammonia reflux released an additional 14% of the radioactivity. No phosalone was present but there were 4 components, two of which were identified as chloroaminophenol and 6-chlorobenzoxazolone accounting for 2% of the applied dose, and 2 unknowns at 4 and 6%. Additional analysis of the remaining soil to determine the distribution of the unextracted radioactivity showed that 13% of the applied radioactivity was associated with humin, 21% with humic acid and 9% with fulvic acid. The KIM modelling programme (Schering AG) was used to calculate degradation values for phosalone and chloroaminophenol and showed a fit criterion of 0.996.

Table 8. Degradation rates of phosalone under anaerobic conditions.

	phosalone		2-amino-5-chlorophenol	
	DT-50, days	DT-90, days	DT-50, days	DT-90, days
Water phase	0.10	1.65	10.15	38.42
Soil phase	4.33	37.93	nc	nc
Entire system	1.82	25.47	29.10	nc

nc: could not be calculated

Phosalone was rapidly taken up by the soil phase and readily degraded in both soil and water. Chloroaminophenol was also readily degraded in anaerobic water and in the system as a whole. Its rate of degradation in soil could not be calculated. The routes of degradation in anaerobic and aerobic soil were similar.

Soil adsorption/desorption

Skinner (1995) reported an adsorption/desorption study of [^{14}C]phosalone in four soils (sandy loam, silty clay loam, loam and clay) by the batch equilibrium method (OECD-TG 106 1981).

[^{14}C]phosalone was applied at concentrations of 0.082, 0.149, 0.424 and 1.0 mg/kg in the silty clay, loam, and clay soils and at 0.076, 0.152, 0.445, and 1.02 mg/kg in the sandy loam. The overall ^{14}C balance for all soils and application rates was 99.5 ± 3.9%. Samples were analysed by TLC and HPLC. Phosalone accounted for >95% of the total radiocarbon in adsorption and desorption solutions of sandy loam and loam soils and >94% in soil pellet extracts of all soils. Phosalone was stable during both adsorption and desorption in sandy loam and loam soils, but was degraded in silty clay loam during adsorption with the formulation of degradation products in solution, and degraded in clay too rapidly to allow quantitative adsorption/desorption measurements. No individual product in any solution or soil extract exceeded 8.5% of the applied radiocarbon. The formation of bound residues was significant in silty clay loam and clay.

The adsorption and desorption coefficients (K_d and K_{oc}) were determined (Table 9). An adsorption isotherm could not be obtained for the clay soil owing to the degradation of phosalone during the adsorptive phase. The adsorption K_d values were found to correlate roughly with the organic carbon content of the soil. The overall average K_{oc} value for adsorption to the three soils for which it could be calculated was 2060. On the basis of the K_{oc} values phosalone is predicted to have only slight to low mobility in soils.

Table 9. Soil characteristics and Freundlich adsorption/desorption constants.

Soil	Organic carbon	Adsorption		First Desorption		Second Desorption	
	%	K_d	K_{oc}	K_d	K_{oc}	K_d	K_{oc}
sandy loam	0.84	22.5	2680	40.0	4760	38.4	4570
silty clay loam	0.71	6.2	870	NA		NA	
loam	1.33	35.1	2640	53.8	4050	51.8	3890
clay	2.95	NA		NA		NA	

NA = not available owing to degradation

Environmental fate in water/sediment systems

Muttzall and de Kreuk (1987) and Muttzall (1995) reported the degradation of phosalone in two water/sediment systems, one from a river and one from a ditch, in biometer flasks over a 12-week period. [^{14}C]phosalone was added to the system at 1.0 mg/l. The level of radioactivity in the water phase decreased from 42% to 10% between week 0 and week 12 in the river system and from 13 to 2% in the ditch system. Radioactivity was mainly associated with the sediment fraction and was rapidly bound. After 1 week in the river system, 22% of the applied ^{14}C was extractable from solids and 59% was bound, 44% and 47% in the ditch system. By the end of the study, 68% and 65% of the applied radioactivity was in bound residues in the river and ditch systems respectively, and $^{14}CO_2$ accounted for 7.9% and 6.9%. Characterization of the products in the aqueous phase showed that phosalone was rapidly degraded, and four unidentified compounds were found. These did not account for more than 10% of the applied radioactivity in either system at the end of the study. The main component in the river system was a polar compound, accounting for 7% of the applied radioactivity, which was not detected in the ditch system. In the sediment phase the main compound found was phosalone, but it did not account for >6% of the applied ^{14}C by the end of the study The 4 compounds found in the water were not present or were at levels ≤1%. Phosalone was rapidly degraded in both the aqueous and sediment phases of both systems.

Bioaccumulation in aquatic organisms

Forbis *et al*. (1986) reported a dynamic 42-day study to evaluate the bioconcentration of [^{14}C]phosalone by bluegill sunfish in a flow-through proportional dilution system which maintained an average concentration of phosalone of 0.93 ± 0.24 µg/l, close to the nominal 1.0 µg/l, throughout the 28-day uptake period. There was a 14-day depuration period. [^{14}C]phosalone was found to be stable in a preliminary equilibration study where 86-109% of the radioactivity was extracted from the water, of which 96% was phosalone and the remainder phosalone oxon.

The minimum quantifiable levels were about 1.5 µg/kg in edible and inedible tissues and whole fish, and 0.34 µg/l in the water. Recoveries from tissues averaged 97-99%.

At the end of the 28-day uptake phase the residues were 0.073, 0.26 and 0.18 µg/g phosalone equivalents in edible tissue, inedible tissue, and whole fish respectively. Residues decreased very rapidly during the depuration phase.

The uptake rate constant (K_1) for whole fish was 0.18 ± 0.02 mg/kg fish/mg/l water/day, and the time to reach 90% of a steady state was 2.4 ± 0.3 days. The depuration rate constant (K_2) was 0.98 ± 0.1, with a half-life for depuration of 0.71 ± 0.08 days. The steady-state bioconcentration factor (BCF) for whole fish was 180 ± 30 according to the non-linear two-compartment kinetic modelling computer programme BIOFAC. During days 14-28 of the uptake phase, the BCF values ranged from 280 to 300 for viscera, 78 to 85 for edible tissue, and 190 to 200 for whole fish.

METHODS OF RESIDUE ANALYSIS

The Meeting received information on methods for the determination of phosalone in crops and soil.

Crops

Residues are generally extracted by macerating with acetone/water 80/20 and cleaned up by partition with dichloromethane. The final extract is concentrated and analysed by gas chromatography.

CNG An No. 4174. This method was used in most supervised trials on crops. Fifty g samples are steeped in water and extracted with acetone. The extract is partitioned with dichloromethane and the final extract is concentrated and analysed by gas chromatography with an NP detector.

In some field trials the procedure was modified by extracting with acetone/water (80/20) instead of steeping in water. The final residue was dissolved in toluene. The LOD is 0.05 mg/kg.

CNG An No. 4765E. This method is used for the determination of phosalone and phosalone oxon. Extraction with acetone is followed by partitioning between water and dichloromethane. Residues are determined by gas-liquid chromatography with an FPD. The LOD is 0.02 mg/kg for both phosalone and phosalone oxon.

CNG An Nos. 4432E and 4698E. Samples are ground with acetone/water (80/20) and partitioned with dichloromethane. The final extract is analysed by gas chromatography with thermionic detection (NPD). The limit of determination is 0.05 mg/kg. The method was validated by analysing untreated control samples and samples spiked at 0.05, 0.25, 0.5, 1 and 2 mg/kg. The mean recoveries from each sample at each level were between 75 and 109% with relative standard deviations less than 20% (Table 10), confirming the repeatability of the method (Gabereau, 1997).

Table 10. Recoveries of phosalone from rape seed, barley and apples.

Commodity	Fortification, mg/kg	No. of analyses	Recovery, %	Mean recovery, %	SD %
Rape seed	0.05	3	82 ,84, 86		
	0.25	3	80, 89, 104	83	9
	1	3	73, 75, 76		
Barley	0.05	3	102, 109, 117		
	0.25	3	99, 100, 100	99	9
	1	3	88, 89, 91		
Apple	0.05	3	86, 88, 94		
	0.5	3	102, 103, 108	98	9
	2	3	99, 101, 101		

Ref. 97-95 (AR 148-97). This is the same as the previous method except that an FPD is used instead of an NPD with confirmation by selective ion-monitoring GC-MS (Bourgade and Yslan, 1988). The limit of determination is 0.05 mg/kg (Table 11).

Table 11. Recoveries of phosalone from apples and rape seed.

Commodity	Fortification, mg/kg	No. of analyses	Recovery, %	Mean recovery, %	SD %
Apple	0.05	3	73, 74, 81	82	6
	0.5	3	86, 87, 89		2
Rape seed	0.5	3	72, 87, 88	82	10

The official method of the Japan Environmental Agency consists in extraction with acetone, partitioning with dichloromethane, and clean-up by Florisil column chromatography with benzene as the eluting solvent. The final extract is analysed by gas chromatography with an NP or FP detector. The limit of detection is 0.01 mg/kg.

The Meeting received information on the multi-residue methods developed by the USFDA (Anon., 1997).

Table 12. Analytical methods used for analysing supervised field trial samples.

Crop	Analytical methods	Reference
Apple	Ref. 4698 (3 Feb 1983)	REF. 25
Apple	see study no. 89-10	REF. 26
Apple	CNG An No 4432E	REF. 27
Apple	CNG An No 4174	REF. 28
Apple	CNG An No 4174	REF. 29
Apple	CNG An No 4174	REF. 30
Apple	CNG An No 4174	REF. 31
Apple	CNG An No 4174	REF. 32
Apple	Japan EA official	REF. 33
Apple	CNG An No 4174	REF. 34
Apple	CNG An No 4432E	REF. 62
Pear	CNG An No 4174	REF. 34
Pear	CNG An No 4174	REF. 35
Pear	modified Japan EA official	REF. 36
Cherry	CNG An No 4698E	REF. 37
Cherry	CNG An No 4174	REF. 38
Cherry	CNG An No 4174	REF. 39
Peach	Ref. 4698 3.Feb. ‘83	REF. 40
Peach	CNG An No 4174	REF. 41
Peach	CNG An No 4174	REF. 42
Peach	CNG An No 4174	REF. 43
Peach	CNG An No 4174	REF. 44
Peach	modified Japan EA official	REF. 45
Peach	Ref. 97-95 (AR 148-97)	REF. 63
Peach	Ref. 97-95 (AR 148-97)	REF. 64
Peach	Ref. 97-95 (AR 148-97)	REF. 65
J-Apricot	modified Japan EA official	REF. 46
Almond	CNG An No 4765E	REF. 47
Almond	CNG An No 4174	REF. 48
Almond	CNG An No 4174	REF. 49
Almond	CNG An No 4174	REF. 50
Almond	CNG An No 4174	REF. 51
Hazelnut	CNG An No 4765E	REF. 52
Hazelnut	CNG An No 4174	REF. 53
Hazelnut	CNG An No 4174	REF. 54
Hazelnut	CNG An No 4174	REF. 55
Hazelnut	CNG An No 4174	REF. 56
Walnut	CNG An No 4765E	REF. 57
Walnut	CNG An No 4174	REF. 58
Walnut	CNG An No 4174	REF. 59
Walnut	CNG An No 4174	REF. 60
Walnut	CNG An No 4174	REF. 61

Soil

Le Gren (1997) described a method for the determination of phosalone and its potential phenoxazone degradation product (2-amino-7-chlorophenoxazin-3-one) in soil. Samples are extracted by distilling with a mixture of water and acetone, and cleaned up on a diol mini-cartridge. Quantification is by GLC with electron capture detection. The limit of determination is 0.02 mg/kg for each compound. The method was validated on four European soils (Chazay, Manningtree, Sevilla, and Bologna) by spiking control samples at 0.02, 0.2, and 2 mg/kg. Individual recoveries ranged from 96 to 115% for phosalone and 68 to 113% for the phenoxazone. The mean recoveries of phosalone and the phenoxazone at each level ranged from 80 to 110% (Table 13).

Table 13. Recoveries of phosalone and aminochlorophenoxazone from soil.

Fortification, mg/kg	Soil	Recovery, %					
		Phosalone			Phenoxazone		
		Individual	mean	SD, %	Individual	mean	SD, %
0.02	Manningtree	107,96,110			102,107,111		
	Sevilla	105,103,101	**102**	**4**	85,110,92	**98**	**15**
	Bologna	101,100,101			110,113,111		
	Chazay	98,103,100			70,83,84		
0.2	Manningtree	110,115,111			70,83,100		
	Sevilla	111,111,111	**110**	**2**	89,81,89	**85**	**15**
	Bologna	108,113,111			94,104,103		
	Chazay	111,104,110			71,70,70		
2	Manningtree	107,106,108			93,77,71		
	Sevilla	102,102,102	**105**	**3**	79,79,84	**80**	**9**
	Bologna	103,101,104			73,68,81		
	Chazay	100,109,111			83,87,87		

Stability of residues in stored analytical samples

Quintelas (1998) reported stability studies on selected crops which showed phosalone to be stable for up to 24 months in macerated samples at -18°C.

Peaches and almonds were spiked with phosalone at 0.5 mg/kg and stored at -18°C for 1 and 3 months. The analytical method was AR 148-97. The mean recoveries after 1 and 3 months respectively were 102 and 94% from peaches and 81 and 79% from almonds. These values were all higher than the initial recoveries at 0.5 mg/kg.

Table 14. Stability of phosalone on peaches and almonds stored at -18°C.

Sample	Storage, months	Fortification, mg/kg	Mean recovery, %	Range, %
Peach	0	0.05	81.5	80-83
	0	0.5	74.5	71-78
	1	0.5	102	93-109
	3	0.5	94	91-96
Almond	0	0.05	89.5	83-96
	0	0.5	77	75-79
	1	0.5	80.7	73-92
	3	0.5	79	72-85

Almonds, apples and cherries containing incurred residues from field studies were analysed after storage at -18°C for 19 to 24 months by method AR 148-97. Recoveries of phosalone were 66 and 77% from almonds, 67 and 70% from apples and 113 and 133% from cherries (Table 15).

Table 15. Stabilities of incurred residues of phosalone in almonds, apples and cherries stored at -18°C.

Sample	Storage, months	Initial residue, mg/kg	Recovery, %	Mean, %
Almond	23	3.39	66	71.5
		4.36	77	
Apple	19	0.75	67	68.5
		0.66	70	
Cherry	24	0.46	133	123
		0.72	113	

Definition of the residue

A metabolism study on apples showed that phosalone was the predominant residue (75-92%) with phosalone oxon at low levels (2-7%) in extracts and rinses of fruit and leaves. In grapes phosalone was also the major residue in the fruit (≥88%) and the oxon was at a very low level (1-2%).

The Meeting concluded that the current definition of the residue as phosalone is suitable both for compliance with MRLs and the estimation of dietary intake.

USE PATTERN

The Meeting received updated information on the registered uses of phosalone on selected crops against leaf eater, leaf roller, tree fly, etc. The information is summarized in Table 16.

Table 16 Registered uses of phosalone in pome fruit, stone fruit and tree nuts. All foliar applications.

Crop	Country	Form	Application			PHI, days
			Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Almond	EU [3]	EC350 g/l	0.75		3	70
Almond	EU [3]	SC500g/l	0.75		3	70
Almond	France [2]	EC350 g/l		0.06-0.07	N	70
Almond	France [2]	SC500 g/l		0.06-0.075	N	70
Apple	Algeria	EC350 g/l	0.6		N	N
Apple	Belgium [2]	SC500 g/l	0.5-0.75	0.05-0.075	N[1]	28
Apple	Canada	SC500 g/l	1.0-1.5	0.03-0.045	3	30
Apple	EU [3]	EC350 g/l	0.6-0.9	0.06	3	28
Apple	EU [3]	WP300 g/l	0.6-0.9	0.06	3	28
Apple	France [2]	EC350 g/l		0.06	N	14
Apple	France [2]	SC500 g/l		0.06	N	15
Apple	Italy [2]	EC350 g/l		0.05-0.07	N	21
Apple	Japan	EC350 g/l		0.023-0.035	2	45
Apple	Japan	EC200 g/l + DDVP		0.02-0.025	2	45
Apple	Netherlands	SC500 g/l	0.6-0.9	0.06	2	28
Apple	Russia	EC350 g/l	0.7-1.4		2	30 (south)
Apple	Russia	EC350 g/l	0.7-1.4		2	40 (north)
Apple	Turkey	EC350 g/l		0.07	N	15
Apple	Ukraine	EC350 g/l	0.7-1.4		2	40
Apricot	EU [3]	EC350 g/l	0.6-0.9	0.06	3	28
Apricot	EU [3]	SC500g/l	0.6-0.9	0.06	3	28
Apricot	France [2]	EC350 g/l		0.06	N	14
Apricot	France [2]	SC500 g/l		0.06	N	15
Apricot	Italy [2]	EC350 g/l		0.05-0.07	N	21
Apricot	Japan	EC200 g/l + DDVP		0.02	2	45
Apricot	Russia	EC350 g/l	0.7-0.84		1	45
Apricot	Ukraine	EC350 g/l	0.7-0.84		1	45
Cherry	Canada	SC500 g/l	1.0-1.5	0.03-0.045	3	14
Cherry	EU [3]	EC350 g/l	0.9	0.06	2	15
Cherry	EU [3]	WP300 g/l	0.9	0.06	2	15
Cherry	France [2]	EC350 g/l		0.06	N	14
Cherry	France [2]	SC500 g/l		0.06	N	15
Cherry	Italy [2]	EC350 g/l		0.05-0.07	N	21
Cherry	Russia	EC350 g/l	0.28-0.98		2	40
Cherry	Turkey	EC350 g/l		0.06	N	15
Cherry	Ukraine	EC350 g/l	0.28-0.98		2	40
Fruit trees	Austria	EC350 g/l		0.05-0.07	N	21
Fruit trees	Croatia	EC350 g/l	7-8.75	0.07-0.875	3	35
Fruit trees	Greece	EC350 g/l		0.05-0.07	N	21
Fruit trees	Hungary	EC350 g/l	0.61		N	21
Fruit trees	Iran	EC350 g/l	N	0.05	N	15
Fruit trees	Iraq	EC350 g/l		0.04-0.06	N	15

Crop	Country	Form	Application			PHI, days
			Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Fruit trees	Kuwait	SC500 g/l		0.06	N	14
Fruit trees	Morocco	EC350 g/l		0.04-0.05	N	15
Fruit trees	Morocco	WP300 g/l		0.045-0.06	N	15
Fruit trees	Poland	EC350 g/l	0.63-0.91	0.06-0.19	2	15
Fruit trees	Spain	WP300 g/l		0.06	N	15
Fruit trees	Tunisia	WP300 g/l		0.04-0.06	N	15
Hazelnut	EU [3]	EC350 g/l	0.6		3	28
Hazelnut	EU [3]	SC500g/l	0.6		3	28
Hazelnut	France [2]	EC350 g/l		0.06	N	21
Hazelnut	France [2]	SC500 g/l		0.06	N	21
Hazelnut	Turkey	EC350 g/l		0.07	N	15
Peach	Canada	SC500 g/l	1.0-1.5	0.03-0.045	3	30
Peach	EU [3]	EC350 g/l	0.6-0.9	0.06	3	28
Peach	EU [3]	SC500g/l	0.6-0.9	0.06	3	28
Peach	France [2]	EC350 g/l		0.06	N	14
Peach	France [2]	SC500 g/l		0.06	N	15
Peach	Italy [2]	EC350 g/l		0.05-0.07	N	21
Peach	Japan	EC200 g/l + DDVP		0.02	2	14
Peach	Russia	EC350 g/l	0.56-0.84		1-2	30-40
Peach	Ukraine	EC350 g/l	0.56-0.84		1-2	30-40
Pear	Algeria	EC350 g/l	0.6		N	N
Pear	Belgium [2]	SC500 g/l	0.5-0.75	0.05-0.075	N[1]	28
Pear	Canada	SC500 g/l	1.0-1.5	0.03-0.045	3	30
Pear	EU [3]	EC350 g/l	0.6-0.9	0.06	3	28
Pear	EU [3]	WP300 g/l	0.6-0.9	0.06	3	28
Pear	France [2]	EC350 g/l		0.06	N	14
Pear	France [2]	SC500 g/l		0.06	N	15
Pear	Italy	EC350 g/l		0.05-0.07	N	21
Pear	Japan	EC350 g/l		0.023-0.035	2	45
Pear	Japan	EC200 g/l + DDVP		0.02	2	45
Pear	Netherlands	SC500 g/l	0.6-0.72	0.06	2	28
Pear	Russia	EC350 g/l	0.7-1.4		2	30 (south)
Pear	Russia	EC350 g/l	0.7-1.4		2	40 (north)
Pear	Taiwan	WP300 g/l	0.3-0.6		1	15
Pear	Ukraine	EC350 g/l	0.7-1.4		2	40
Plum	Canada	SC500 g/l	1.0-1.5	0.03-0.0625	3	30
Plum	EU [3]	EC350 g/l	0.6-0.9	0.06	3	28
Plum	EU [3]	SC500g/l	0.6-0.9	0.06	3	28
Plum	France [2]	EC350 g/l		0.06-0.07	N	14
Plum	France [2]	SC500 g/l		0.06-0.07	N	15
Plum	Italy [2]	EC350 g/l		0.05-0.07	N	21
Plum	Russia	EC350 g/l	0.28-0.98		2	40
Plum	Turkey	EC350 g/l		0.07	N	15
Plum	Ukraine	EC350 g/l	0.28-0.98		2	40
Pome fruit	Slovak Republic	EC350 g/l		0.07	N	21
Pome fruit	Switzerland	EC350 g/l	0.79-1.05	0.05	N	30
Prune	Canada	SC500 g/l	1.0-1.5	0.03-0.0625	3	30
Stone fruit	Algeria	EC350 g/l	0.6		N	N
Stone fruit	Czech Republic	EC350 g/l		0.07	N	21
Stone fruit	EU	EC350 g/l	0.9	0.06	3	28
Stone fruit	EU	WP300 g/l	0.9	0.06	3	28
Stone fruit	Slovak Republic	EC350 g/l		0.07	N	21
Stone fruit	Switzerland	EC350 g/l	0.79-1.05		N	N
Walnut	EU [3]	EC350 g/l	0.6			
Walnut	EU [3]	SC500g/l	0.6			
Walnut	France	EC350 g/l		0.06	N	21
Walnut	France	SC500 g/l		0.06	N	21

N: not specified
In France, standard orchard spray volume is 10 hl/ha.
[1] Used in integrated pest management (IPM) programmes, rarely exceeding 2 applications
[2] Currently registered national labels for countries within the EU Member States will be revised in the future to reflect GAP to be supported at the EU level
[3] Use pattern envisaged at EU level in anticipation of the future registration requirements.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Information received on supervised field trials on apples, pears, peaches, Japanese apricots, cherries, almonds, hazelnuts and walnuts is summarized in Tables 17-24.

Table 17	*Apples.* Italy, France, Japan, Germany
Table 18	*Pears.* Spain, Japan
Table 19	*Cherries*. France
Table 20	*Peaches*. Italy, France, Spain, Japan
Table 21	*Japanese Apricots*. Japan
Table 22	*Almonds*. France
Table 23	*Hazelnut.* France
Table 24	*Walnuts*. France

Where residues were not detected they are shown as below the limit of determination (LOD), e.g. <0.01 mg/kg.

References to supervised trials will be found in the second (numerical) reference list.

Apples. Phosalone was applied by experimental backpack sprayers in France and Germany and by pressure sprayers in Italy and Japan. Plots in the French trials were 3 to 6 trees and field samples of twelve fruit or >2 kg were stored frozen for 2 to 10 months before analysis. In Italy plots were 4 to 10 trees, field samples were twelve fruit, and storage was 1 to 4 months before analysis. In Germany 4 trees per plot and samples of 12 apples with storage for 5 to 7 months before analysis. In Japan only one tree was treated and 4 to 6 kg samples were stored for 3 months before analysis.

Table 17. Phosalone residues in apples resulting from supervised trials in Italy, France, Japan and Germany. Analyses of replicate field samples are shown separately. Double underlined residues are from treatments according to GAP.

Country, Year, Location	Form.	Application				Variety	PHI days	Residues mg/kg		Ref./Report no.
		No.	kg ai/ha	water l/ha	kg ai/hl			Mean	Individual	
Italy, 1989	EC 232 g/l	4	0.6	1000	0.06	Rome Beauty	0 7 14 21 28 35	1.6 1.0 1.1[1] 0.5 0.4 0.6[2]		Ref. 25 AG/CRLD/AN/8916827
Italy, 1989	EC 24%	5	0.6	1000	0.06	Rome Beauty	21	0.65[2]		Ref. 26 AG/CRLD/AN/9015907
		5	0.6	1000	0.06	Red Chief	21	0.85[2]		
		9	1.2	2000	0.06	Red Chief	21	0.96[2]		
France, 1995 Saran	SC 500 g/l	1	0.88	563	0.16	Golden	2 h 3 7 14		0.69,0.72 0.67,1.3 0.54,1.4 0.78,1.1	Ref. 27 R&D/CRLD/AN/kd/9616621
Souastre		1	0.88	560	0.16	Idared	2 h 3 7		1.1,1.4 1.2,2.6 1.3,1.9	

Country, Year, Location	Form.	Application				Variety	PHI days	Residues mg/kg		Ref./Report no.
		No.	kg ai/ha	water l/ha	kg ai/hl			Mean	Individual	
							14		0.49,1.6	
St. Laurent d`Agng		1	0.87	583	0.15	Elstar	2 h 3 7 14		1.0,1.4 1.2,1.8 1.7,1.6 2.5,1.5	
Lavaur		1	0.88	1143	0.08	Grany	2 h 3 8 14		0.71,0.45 0.54,0.54 0.49,0.58 0.38,0.17	
France, (South) 1996 Beaucaire	EC 350 g/l	3	0.61	983	0.06	Golden	16 22 31 45	0.70 0.68 0.74[1,2] 0.58		Ref. 28 R&D/CRLD/AN/dbe/9 716155
France (North), 1996 Tigy	EC 350 g/l	3	0.6	810	0.07	Idared	14 19 29 44	0.66[1] 0.52 0.45 0.37		Ref. 29 R&D/CRLD/AN/vt/97 16613
France (South), 1996 Seyssuel		3	0.61	833	0.07	Golden	15 21 30 45	0.99 1.1 1.5[1,2] 1.1		
France (North), 1997 Crops Nuds	EC 350 g/l	3	0.74	545	0.14	Indaine	27		1.0,1.2	Ref. 30 R&D/CRLD/AN/vt/98 15382
France (South), 1997 Eyragues		3	0.74	872	0.08	Golden	27		0.82,0.87	
France (North), 1997 Crops Nuds	EC 350 g/l	3	0.73	538	0.14	Indaine	2 h 11 18 24 31 38	1.4 1.0 1.0 0.7 0.6 0.43		Ref. 31 R&D/CRLD/AN/dbe/9 815324
France (South), 1997 Seyssuel		3	0.61	740	0.08	Golden	2 h 14 21 28 35 42	0.93 0.88 0.77 0.63 0.65 0.64		
Italy, 1997 Bologna	WP 291 g/kg	3	0.90	1500	0.06	Golden delicious	21 28	0.88 0.91[2]		Ref. 32 R&D/CRLD/AN/vt/98 15916
Japan, 1979 Fuku-shima	EC 35%	2(3)[3]	1.8	5000	0.035	Starking Delicious	45	0.42		Ref. 33
							60	0.20		
		3(4)[3]					45 60	0.52 0.59		
Nagano		2	1.8	5000	0.035	Fuji	43 57	0.58 0.52		
		3					43 57	0.82 0.78		
Germany (North), 1997 Berlin[4]	WP 304 g/kg	3			0.06	Jonathan	0 7 14 21 28	3.0 2.7 2.5 0.97 0.84		Ref. 34 R&D/CRLD/AN/msa/9 816476

Country, Year, Location	Form.	Application				Variety	PHI days	Residues mg/kg		Ref./Report no.
		No.	kg ai/ha	water l/ha	kg ai/hl			Mean	Individual	
							35	0.063		
Germany (North), 1997 Sollingen		3	0.92	1515	0.06	Jonagold	0 15 21 28 35 42	0.73 0.43 0.45 <u>0.46</u>[1] 0.35 0.29		

[1] According to French GAP
[2] According to Italian GAP
[3] 2 or 3 treatments were intended but one support treatment was also applied, owing to rainfall
[4] This trial was reported to have been at the GAP spray concentration of 0.06 kg ai/hl but the measurement of the spray volume, which was close to 4 l/tree, was suspect

<u>Pears</u>. Phosalone was applied by experimental backpack sprayers in Spain and Germany and by pressure sprayers in Japan. The plot sizes were 16 m^2 (4 trees) in Japan, 25.6 m^2 (4 trees) in Spain and 70 m^2 (4 trees) in Germany. Field samples were twelve pears in Germany and Spain and 4 kg in Japan, and were stored in the freezer for 1 to 7 months before analysis.

Table 18. Phosalone residues in pears resulting from supervised trials in Germany, Spain and Japan. Underlined and double underlined residues are from treatments according to GAP. Double underlined residues were used to estimate maximum residue and STMR levels.

Country, Year	Form.	Application				Variety	PHI, days	Mean residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	water l/ha	kg ai/h				
Germany, 1997	WP	3	0.89	1485	0.061	Conference	29	0.49	Ref. 34 R&D/CRLD/AN/msa/9816476
							35	0.63	
Spain, 1997	WP 300g/kg	3	0.90	1250	0.072	Conference	0 15 21 30 45	0.93 <u>0.38</u>[1] <u>0.36</u>[2] 0.23 0.13	Ref. 35 R&D/CRLD/AN/vt/9815818
Japan, 1989	EC 35%	2	1.75	5000	0.035	Kousui	45 60	<u>0.11</u>[3] 0.033	Ref. 36
		2	2.19	6250	0.035	Cyojuro	45 60	<u>0.29</u>[3] 0.099	

[1] According to French GAP
[2] According to Italian GAP
[3] According to Japanese GAP

<u>Cherries</u>. Trees were sprayed with an experimental atomizer with spray boom, backpack and tree sprayers in supervised trials in France. Plots sizes ranged from 12.75 m^2 to 81 m^2 and 500 to 1000g of field samples were collected and stored frozen for 3 to 9 months before analysis.

Table 19. Phosalone residues in cherries resulting from supervised trials in France. Analyses on replicate field samples in each trial are shown separately. Double underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Year, Location	Form.	Application				Sample (Variety)	PHI, days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	Water, l/ha	kg ai/hl				
1994 St.Didier sous	SC 500g/l	3	0.75	769	0.098	fruit with stone (Starking)	14	<u>1.2, 1.4</u>	Ref. 37 R&D/CRLD/An/fb/9515875

Year, Location	Form.	Application				Sample (Variety)	PHI, days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	Water, l/ha	kg ai/hl				
		3	1.1	769	0.15	fruit with stone (Starking)	14	1.6, 3.4	
Blauvac		3	0.74	497	0.15	fruit with stone (Van)	14	1.6, 1.3	
		3	1.1	505	0.22	fruit with stone (Van)	14	1.8, 2.5	
St. Simplice		3	0.87	993	0.088	fruit with stone (Sumbeurs)	11	1.5, 1.8	
		3	1.4	1345	0.1	fruit with stone (Sumbeurs)	11	1.5, 3.1	
(South),1996	SC 500g/l	1	0.6	300	0.2	fruit with stone (Sunburst)	11	0.34, 0.37	Ref. 38 R&D/CRLD/AN /dbe/9716189
Meilhan							16 21	0.59, 0.23 0.23, 0.17	
		2	0.6	300	0.2	fruit with stone (Sunburst)	11 16 21	0.61, 0.78 0.46, 0.72 0.43, 0.41	
(North), 1996 Mezieres		1	0.59	803	0.073	fruit with stone (Burlat)	8 14 18	0.51, 0.5 0.35, 0.21 0.47, 0.32	
		2	0.59	801	0.073	fruit with stone (Burlat)	8 14 18	0.53, 0.6 0.45, 0.31 0.13, 0.33	
(North), 1996 Olivet		1	0.58	653	0.089	fruit with stone (Duroni 3)	9 15 23	0.58, 0.69 0.26, 0.26 0.08, 0.15	
		2	0.58	650	0.089	fruit with stone (Duroni 3)	9 15 23	0.60, 0.63 0.23, 0.22 0.14, 0.08	
(South),1996 St. Didier		1	0.60	500	0.12	fruit with stone (Burlat)	10 17 21	0.33, 0.33 0.18, 0.16 0.15, 0.08	
		2	0.60	416	0.14	fruit with stone (Burlat)	10 17 21	0.45, 0.6 0.15, 0.26 0.12, 0.2	
(South),1996		1	0.60	667	0.09	fruit with stone (Duroni 2)	15	0.22, 0.28	
Blcuvac							20 26	0.14, 0.3 0.10, 0.14	
		2	0.60	667	0.09	fruit with stone (Duroni 2)	15 20 26	0.27, 0.42 0.17, 0.22 0.14, 0.17	
(South),1996 Belcaste		1	0.60	400	0.15	fruit with stone (Stark)	11 14 20	0.17, 0.16 0.15, 0.6 0.53, 0.22	
		2	0.60	400	0.15	fruit with stone (Stark)	11 14 20	0.62, 0.56 0.37, 0.46 0.15, 0.36	
(North),1997 Villeveque	EC 353g/l	1	0.56	935	0.06	fruit (Lapins)	10 15 21	0.36, 0.24 0.36, 0.18 0.11, 0.12	Ref. 39 R&D/CRLD/AN /vt/9815381
		2	0.58	965	0.06	fruit (Lapins)	10 15	0.36, 0.32 0.29 ,0.2	
							21	0.13, 0.13	

Peaches. Trees were sprayed with a hand-gun motor pump and pressure spray in Italian and Japanese trials, and with backpack sprayers and air blast sprayers in France. Plots were 4 to 10 trees in Italy, 45 to 90 m^2 with 2 to 6 trees in France, 100 m^2 in Spain and 1 or 2 trees in Japan. Field samples of 500 g or 12 peaches were stored frozen for 2 to 6 months before analysis.

Table 20. Phosalone residues in peaches resulting from supervised trials in Italy, France, Spain and Japan. Replicate individual residues are from replicate field samples. Double underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Country, Year	Form.	Application				Sample (Variety)	PHI days	Residues, mg/kg		Ref.
		No.	Kg ai/ha	waterl /ha	kg ai/hl			Mean	Individual	
Italy, 1989	EC 232 g/l	1	1.2	2000	0.06	Fruit (Starkred Gold)	0 7 14 21 28	0.4 0.3 <u>0.16</u>[1] <u>0.13</u>[2] 0.13		Ref. 40 AG/CRLD/AN/ 8916828
France, 1997 (South)	EC 350 g/l	3	0.74	563	0.13	Fruit without stone (Alexandra)	2 h 14 21 28 35		1.5,1.6 0.80,0.52 0.57,0.61 0.53,0.76 0.54,0.49	Ref. 41 R&D/CRLD/AN /dbe/9815342
						Fruit (whole)	2h 14 21 28 35		1.4, 1.5 <u>0.73</u>[1], 0.48 0.53, 0.57 0.48, <u>0.68</u>[2] 0.5, 0.45	calculation
France, 1997 (South) Ste Bazeille	EC 350 g/l	3	0.61	288	0.21	Fruit without stone (Royal glory) Fruit (whole)	26 26		0.44,0.29 0.37,0.28 0.41, 0.27 0.35, 0.26	Ref. 42 R&D/CRLD/AN /vt/9815817 calculation
Italy, 1997	WP 291 g/kg	3	0.88	1500	0.06	Fruit (whole) (Duchessa d'Este) Pulp	0 14 21 28 35 35	3.7 <u>1.5</u>[1] <u>1.4</u>[2] 0.71 0.45 0.49	calculation	Ref. 43 R&D/CRLD/AN /dbe/9815848
Spain, 1997	WP 300 g/kg	3	0.9	800	0.11	Fruit without stone (Red Top) Fruit (whole)	28 28	0.54 0.51	calculation	Ref. 44 R&D/CRLD/AN /dbe/9815325
Japan, 1982 Fuku-shima	EC 20%	2	0.8	4000	0.02	Fruit without stone & peeled (Ohkubo)	15 30 45	0.09 0.02 <0.01		Ref. 45
						Peel	15 30 45	8.92 3.93 1.20		
						Fruit without stone	15	2.3	calculation	
							30 45	0.88 0.25		
Ishikawa						Fruit without stone & peeled (Ohkubo)	15 30 45	0.04 0.02 <0.01		
						Peel	15 30 45	5.43 3.62 1.02		
						Fruit without stone	15 30 45	1.33 0.63 0.17	calculation	

Country, Year	Form.	Application				Sample (Variety)	PHI days	Residues, mg/kg		Ref.
		No.	Kg ai/ha	waterl /ha	kg ai/hl			Mean	Individual	
France, 1998 (South) Subirats	WP 298 g/kg	3	0.89	800	0.11	Fruit without stone (Baby Gold 6)	0 15 21 30 45	0.72 0.50 0.27 0.35 0.49		Ref. 63 R&D/CRLD/AN /mr/9915513
						Fruit (whole)	0 15 21 30 45	0.65 --- 0.25 0.32 0.45	calculation	
France, 1998 (South) Charly	EC 350 g/l	3	0.76	351	0.22	Fruit without stone (Redwing) Fruit (whole)	26 26		0.24,0.68 <u>0.22</u>, <u>0.63</u>[2]	Ref. 64 R&D/CRLD/AN /mr/9915763 calculation
France, 1998 (South)	EC 350 g/l	3	0.76	571	0.13	Fruit without stone (Manon)	2 h 10 17 24 31	 0.33 0.12	0.81,0.54 0.30,0.35 0.13,0.37	Ref. 65 R&D/CRLD/AN /mr/9915759
						Fruit (whole)	2 h		0.78, 0.52	calculation
							10 17 24 31	 0.31 0.11	0.29, 0.33 <u>0.12</u>, <u>0.35</u>[1]	

[1] According to French GAP
[2] According to Italian GAP

<u>Apricots.</u> Trees were treated by motor pump sprayers in Japan. Plots consisted of 2 and 3 trees and 4 kg field samples were stored frozen for 2 to 3 months before analysis.

Table 21. Phosalone residues in Japanese apricots resulting from a supervised trial in Japan. Underlined residues are from treatments according to GAP.

Year	Form.	Application				Sample (Variety)	PHI, days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	water l/ha	kg ai/hl				
1982	EC 20%	2	0.8	4000	0.02	Fruit without stone (Shiro Kaga)	21 32 47	0.046 0.044 <u>0.009</u>	Ref. 46
		2	0.8	6000	0.02	Fruit without stone (Seigyoku)	21 30 45	0.724 0.698 <u>0.005</u>	

<u>Almonds.</u> Trees were treated with phosalone by experimental atomizer with spray boom and backpack sprayers in supervised trials in France. Plots sizes ranged from 105 m^2 to 140 m^2 with 3 or 4 trees/plot. Field samples of 1000 g were collected and stored frozen for 3 to 8 months before analysis.

Table 22a. Phosalone residues in almonds resulting from supervised trials in Southern France. Analyses of replicate field samples in each trial are shown separately. Double underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Location Year	Form	Application				Sample (Variety)	PHI days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	Water l/ha	kg ai/hl				
1994 St Gilles	SC 500g/l	3	0.75	143	0.52	nut without husk (Ferragnes)	27	<0.02, <0.02	Ref. 47 R&D/CRLD/AN/bd/9516513
		3	1.1	143	0.79		27	<0.02, <0.02	
Ventenac		3	0.75	857	0.09		14	<0.02, <0.02	
		3	1.1	857	0.13		14	0.022, 0.028	
1996 St.Gilles	EC	3	0.77	215	0.36	kernel (Lauranne)	78	<u>≤0.05, ≤0.05</u>	Ref. 48 R&D/CRLD/AN/dbe/9716150
1996 St.Gilles	EC	3	0.77	215	0.36	shell & kernel (Ferragnes) kernel	2 h 29 42 78	4.1, 4.6 2.6, 3.2 3.2, 2.0 <u>≤0.05, ≤0.05</u>	Ref. 49 R&D/CRLD/AN/dbe/9716168
1996 Ventenac	SC 500g/l	3	0.75	571	0.13	nut (Ferragnes)	76	<u>≤0.05</u>, <0.05	Ref. 50 R&D/CRLD/AN/kd/9716028
1996 St.Gilles	SC 500h/l	3	0.75	215	0.35	nut (Ferragnes) kernel	2 h 29 42 78	4.7, 4.5 4.1, 4.4 3.4, 4.4 <u>≤0.05, 0.074</u>	Ref. 51 R&D/CRLD/AN/dbe/9716188

Table 22b. Residues of phosalone oxon in almonds.

Year, location	Form.	Application				Sample (Variety)	PHI days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	water l/ha	kg ai/hl				
1994 St Gilles	SC 500g/l	3	0.75	143	0.52	nut without husk (Ferragnes)	27	<0.02	Ref. 47 R&D/CRLD/AN/bd/9516513
		3	1.1	143	0.79		27	<0.02	
		3	0.75	857	0.09		14	<0.02	
		3	1.1	857	0.13		14	<0.02	

<u>Hazelnuts</u>. Trees were sprayed with phosalone by experimental atomizer with spray boom and backpack sprayers in supervised trials in France. Plots sizes were 45 m^2 to 108 m^2 with 3 to 8 trees/plot. Field samples of 1000g (900g in one trial) were stored frozen for 6 to 8 months before analysis.

Table 23a. Phosalone residues in hazelnuts resulting from supervised trials in Southern France. Analyses of replicate field samples in each trial are shown separately. Double underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Year, location	Form.	Application	Sample	PHI,	Residues, mg/kg	Ref./Report no.

		No.	kg ai/ha	Water l/ha	kg ai/hl	(Variety)	days		
1994 Guitinieres	SC 500g/l	3	0.75	200	0.38	without cup (Ennis)	13	0.026, 0.039	Ref. 52 R&D/CRLD/AN/bd/9515930
		3	1.1	200	0.56		13	0.077, 0.067	
Pollionnay		3	0.75	800	0.09	without cup (Merveille de Bollwiller)	14	0.071, 0.036	
		3	1.1	933	0.12		14	0.079, 0.068	
1996 Pollionnay	SC 500g/l	2	0.6	778	0.08	nuts (Merveille de Bollwiller) kernel without shell	2 h 7 14 21	7.2,6.0 0.061, 0.064 <0.05(2) <u>≤0.05</u>(2)	Ref. 53 R&D/CRLD/AN/dbe/9716158
1996 Puechoursi	EC 350g/l	2	0.61	556	0.11	kernel without shell (Fertile de Coutard)	20	<u>≤0.05</u>(2)	Ref. 54 R&D/CRLD/AN/dbe/9716157
1996 Villesequelande	SC 500g/l	2	0.60	667	0.09	kernel without shell (Merveille de Bollwiller)	22	<u>≤0.05</u>(2)	Ref. 55 R&D/CRLD/AN/dbe/9716159
1996 Guitineres	EC	2	0.61	800	0.08	nuts (Ennis) kernel without shell	2 h 7 13 21	2.3,2.7 0.82,0.76 0.63,0.70 <u>≤0.05</u> (2)	Ref. 56 R&D/CRLD/AN/dbe/9716229

Table 23b Residues of phosalone oxon in hazelnuts.

Country Year	Form.	Application				Sample (Variety)	PHI, days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	Water l/ha	kg ai/hl				
France, 1994	SC	3	0.75	200	0.38	without cup (Ennis)	13	<0.02	Ref. 52 R&D/CRLD/AN/bd/9515930
			1.1	200	0.56		13	<0.02	
			0.75	800	0.09	without cup	14	<0.02	
			1.1	933	0.12		14	<0.02	

<u>Walnuts</u>. Trees were sprayed with phosalone by experimental atomizer with spray boom and backpack sprayers in supervised trials in France. Plots sizes were 49 m^2 to 400 m^2 with 3 to 4 trees/plot. Field samples of 1000 g (1.5 kg in one trial) were stored frozen for 5 to 11 months before analysis.

Table 24. Phosalone residues in walnuts resulting from supervised trials in Southern France. Analyses of replicate field samples in each trial are shown separately. Double underlined residues are from treatments according to GAP and were used to estimate maximum residue and STMR levels.

Year Location	Form.	Application				Sample (Variety)	PHI, days	Residues, mg/kg	Ref./Report no.
		No.	kg ai/ha	Water, l/ha	kg ai/hl				
1994 Barret	SC 500g/l	3	0.75	146	0.51	kernel (Franquette)	14	<0.02(2)	Ref. 57 R&D/CRLD/AN/bd/ 9515931
		3	1.1	150	0.75		14	<0.02(2)	
Chatte		3	0.75	530	0.14	kernel (Chico)	14	0.18,0.14	
		3	1.1	530	0.21		14	0.13,0.15	
1996 Marches	EC 350g/l	4	0.41	232	0.18	kernel (Franquette)	2 h	<0.05(2)	Ref. 58 R&D/CRLD/AN/vt/9 716585
						whole walnut (nut, shell & hull)	7	1.3,1.8	Ref. 58 R&D/CRLD/AN/981 7001
						whole walnut (nut, shell & hull)	14	0.81,0.89	Ref. 58 R&D/CRLD/AN/981 7001
						kernel	21	<0.05, 0.055	Ref. 58 R&D/CRLD/AN/vt/9 716585
1996 Marches	SC 500g/l	4	0.40	233	0.17	kernel (nut) (Franquette)	21	0.19,0.09 0.16,0.09	Ref. 59 R&D/CRLD/AN/vt/9 716568
1996 La Lustre	EC 350g/l	4	0.61	141	0.43	kernel (nut) (Franquette)	28	<0.05(2)	Ref. 60 R&D/CRLD/AN/vt/9 716561
1996 La Lustre	SC 500g/l	4	0.61	141	0.43	kernel (nut) (Franquette)	2 h	<0.05(2)	Ref. 61 R&D/CRLD/AN/dbe /9716595
							7	<0.05, 0.052	
							14	<u>≤0.05</u>(2)	
							28	<0.05(2)	

RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

<u>Apples</u>. In a processing trial according to commercial practice (Maestracci, 1999) apples were treated four times at an application rate of 0.6 kg ai/ha with 300 l/ha of an SC formulation. Samples taken 76 days after the last application were processed into compote and pulp.

To produce compote, the apples were peeled by rotating knives, cooked for 10 min. at 100 °C, then stored in holding tanks at 80°C for 1 to 3 h. Samples were filtered, combined with sugar etc. and heated first at 105°C, then at 92°C, before packing as infant food.

About 86% of the phosalone was lost during processing into compote (Table 25).

Table 25. Effect of processing on phosalone residues in apples.

Sample	Mean residue, mg/kg	Processing factor
Whole apple	0.19	1.00

Sample	Mean residue, mg/kg	Processing factor
Peeled apple	0.13	0.68
Unpeeled, washed apple	0.20	1.05
Boiled pulp from peeled apple	0.030	0.16
Boiled pulp from unpeeled washed apple	0.055	0.29
Compote from whole apple	0.026	0.14
Compote from unpeeled washed apple	0.054	0.28

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was informed of the national MRLs shown in the Table below.

Country	MRL, mg/kg	Commodity
Austria	1	Fruit except pome fruit and peach
	2	Peach
Belgium	2	Peach, pome fruit
Belarus	0.2	Pome and stone fruit
Bulgaria	2	Apple
Canada	2	Pear
	4	Apricot, peach
	5	Apple, plum
	6	Cherry
	12	Apricot (dried)
Croatia	2	Fruit
Czech Republic	2	Apple, stone fruit
Finland	2	Peach, pome fruit
France	0.1	Almond, hazelnut
	0.2	Walnut
	2	Pome fruit, stone fruit (including cherry)
Hungary	1	Fruit
India	0.5	Fruit except pears and citrus fruit
	2	Pear
Italy	2	Peach, pome fruit
Japan	1	Fruit (general)
Luxemburg	2	Peach, pome fruit
Macedonia	2	Apple, peach
Moldavia	0.2	Pome and stone fruit
Netherlands	1	Fruit except peach and pome fruit
	2	Peach, pome fruit
Poland	0.1	Fruit except strawberry, citrus fruit
Russia	0.2	Pome and stone fruit
Spain	2	Pome and stone fruit
Sweden	2	Peach, pome fruit
Switzerland	2	Peach, pome fruit
Taiwan	1	Pear
Turkey	0.5	Peach, plum, cherry
UK	2	Peach, pome fruit
Yugoslavia	2	Apple, peach

APPRAISAL

Phosalone was the subject of a periodic review of residues by the 1994 JMPR. That Meeting concluded that the existing CXLs for phosalone should be withdrawn, owing to inadequacies in the available information. The CCPR decided to maintain the CXLs for 4 years. A periodic review of the toxicology was carried out by the 1997 JMPR, which allocated an ADI of 0-0.02 mg/kg bw.

The Meeting received new or revised information on physical and chemical properties, metabolic and environmental fate, analytical methods, stability of analytical samples, use patterns, supervised trials, apple processing, and national MRLs. A new determination of the octanol/water partition coefficient gave a value of log P_{ow} = 4.01 at 20°C.

Plant metabolism

Phosalone was typically the main residue; phosalone oxon and 6-chlorobenzoxazolone were found at low levels in apples. In grapes, phosalone was the main residue in the juice and constituted more than 95% of the residue in the pulp.

Environmental fate

Photolysis. In water at pH 5, decomposition is very rapid (half-life 15-20 minutes). The quantum yield at 300 nm for phosalone in aqueous solution was determined to be 0.19. In the troposhere the estimated reaction constant at 298° K is 9.34 x 10^{-3} s^{-1} which corresponds to a half-life of about 74 daylight seconds.

Biodegradability. In active sludge about 20% of the initial radioactivity of [^{14}C]phosalone was detected as $^{14}CO_2$ after six weeks.

Aerobic degradation in soil. Phosalone was degraded rapidly with a half-life of 2.9 days. Unextracted radiocarbon increased to an average of 85% by 30 days. The product phenoxazone was observed but did not exceed 1.5% of the applied radioactivity.

Anaerobic degradation in soil. In the water phase, phosalone was rapidly degraded to 2-amino-5-chlorophenol which reached a maximum of 20% of the applied radioactivity after 3 days, then decreased. In the soil phase phosalone was also rapidly degraded, producing chloroaminophenol which reached a maximum of 8% of the applied radioactivity after 14 days.

Soil adsorption/desorption was studied in sandy loam, silty clay loam, loam and clay. The average K_{oc} value for adsorption on the three loam soils was 2060. Degradation on clay was too rapid to measure adsorption. Phosalone is predicted to have slight to low mobility in soils.

Environmental fate in water/sediment systems. In river and ditch systems 68% and 65% of the applied radioactivity was bound after 12 weeks. In the aqueous phases four degradation products were found but not identified. They did not exceed 10% of the applied radioactivity. In the sediment phosalone was the main residue, but did not exceed 6% of the applied radioactivity.

Bioaccumulation. A dynamic 42-day study was conducted to determine the uptake of radiolabelled phosalone by bluegill sunfish. The uptake rate constant for whole fish was 0.18 (± 0.02) mg/kg fish/mg/l water/day. The bio-concentration factors were 280 to 300 for viscera, 78 to 85 for edible tissue and 190 to 200 for whole fish.

Analytical methods. In general residues are extracted with acetone/water and cleaned up by liquid-liquid partition with dichloromethane. The final extract is concentrated and analysed by GLC with EC, NP or FP detection. There are several variants.

A number of residue analytical methods were described in the 1994 JMPR monograph. The LODs for plants were generally 0.05 mg/kg with an ECD, FPD or NPD.

In a more recent method for phosalone and phosalone oxon the residues are extracted with acetone and cleaned up by partitioning between water and dichloromethane. Quantification is with an FPD. The LODs are 0.02 mg/kg for both compounds.

Stability of residues on stored analytical samples. Fortified peaches and almonds were stored frozen at −8°C for 1 and 3 months. Recoveries after storage were 94 to 102% from peaches and 79 to 81% from almonds. Almonds, apples and cherries with incurred residues were stored at −18°C for 19 to 24 months. The recovery of phosalone was 66 to 77% from almonds, 67 to 70% from apples and 113 to 133% from cherries.

Definition of the residue

The current definition of the residue is "phosalone". A metabolism study on apples showed that phosalone was the predominant residue (75%-92%) with only 2%-7% of the oxon. In grapes phosalone was about 90% or more of the residue with only 1-2% of the oxon. The Meeting concluded that the current residue definition is suitable both for compliance with MRLs and for the estimation of dietary intake.

The octanol-water partition coefficient (log P_{ow} = 4.01) suggests fat-solubility. The Meeting concluded that phosalone is fat-soluble.

Residues resulting from supervised trials

Pome fruits. Phosalone may be used at 0.06 kg ai/hl (0.6 kg ai/ha, standard orchard spray volume: 1000 l/ha) on apples and pears in France with a PHI of 14 days for EC, 15 days for SC. The residues in apples and pears from 5 French, 1 German, 1 Italian and 1 Spanish trials meeting these conditions were 1.1, 0.38, 0.74, 0.66, 1.5, 1.0, 0.46 and 0.38 mg/kg.

In Italy, phosalone may be used at 0.05-0.07 kg ai/hl on apples and pears with a PHI of 21 days. Several of the trials complied with both French and Italian GAP. The residues from 5 Italian, 3 French and 1 Spanish trials meeting these conditions were 0.6, 0.65, 0.85, 0.96, 0.74, 0.52, 1.5, 1.0, 0.91 and 0.36 mg/kg.

Phosalone residues in apples and pears from the 5 Italian, 5 French, 1 German and 1 Spanish trials in rank order (median underlined) were 0.38 (2), 0.46, 0.65, 0.66, 0.74, 0.85, 0.91, 0.96, 1.0, 1.1 and 1.5 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.8 mg/kg for phosalone in pome fruits.

Stone fruits. Phosalone may be used on cherries and peaches in France at 0.06 kg ai/hl (0.6 kg ai/ha) with a PHI of 14 days. The residues from 16 trials on cherries and 4 on peaches meeting these conditions were 0.18-1.6 mg/kg and 0.16-1.5 mg/kg respectively. The trials on peaches also complied with Italian GAP: 0.06-0.07 kg ai/hl with a PHI of 21 days. The residues in peaches from 2 Italian and 4 French trials meeting these conditions were 0.13, 0.68, 1.4, 0.45, 0.63 and 0.31 mg/kg.

The Meeting concluded that the residues in cherries and peaches belonged to the same population.

The residues in cherries and peaches from the French and Italian trials in rank order (median underlined) were 0.16, 0.18, 0.23, 0.26(2), 0.29, 0.3, 0.35, 0.36, 0.42, 0.45 (2), 0.46, 0.47, 0.59, 0.6, 0.63, 0.72, 0.73, 1.4, 1.5 and 1.6 mg/kg.

Apricots. Phosalone may be used at 0.02 kg ai/hl on Japanese apricots in Japan with a PHI of 45 days. The residues in Japanese apricots from 2 trials in Japan meeting these conditions were 0.005 and 0.009 mg/kg.

The Meeting estimated a maximum residue level of 2 mg/kg and an STMR of 0.45 mg/kg for phosalone on stone fruits.

Tree nuts. Phosalone may be used on almonds in France at 0.06-0.075 kg ai/hl (0.60-0.75 kg ai/ha) with a PHI of 70 days. The residues in almonds from 6 French trials meeting these conditions in rank order (median underlined) were <0.02 (2), <0.05 (3) and 0.074 mg/kg.

The Meeting estimated a maximum residue level of 0.1 mg/kg and an STMR of 0.05 mg/kg for phosalone in almonds.

Phosalone may be used on hazelnuts and walnuts in France at 0.06 kg ai/hl (0.60 kg ai/kg) with a PHI of 21 days. The residues in hazelnuts from 4 French trials and in walnuts from 1 French trial meeting these conditions were all <0.05 mg/kg.

The Meeting estimated a maximum residue level of 0.05* mg/kg and an STMR of 0.05 mg/kg for phosalone in hazelnuts and walnuts.

Processing

Apples were processed to compote with a processing factor of 0.14. As the STMR for pome fruits is 0.8 mg/kg the Meeting estimated an STMR of 0.1 mg/kg for phosalone in apple compote.

RECOMMENDATIONS

On the basis of data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue for compliance with MRLs and for estimation of dietary intake: phosalone. The residue is fat-soluble.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
TN 0660	Almonds	0.1	-	0.05
	Apple compote		-	0.1
TN 0666	Hazelnuts	0.05*	-	0.05
FP 0009	Pome fruits	2	-[1]	0.8
FS 0012	Stone fruits	2	-	0.45
TN 0678	Walnuts	0.05*	-	0.05

[1]A CXL of 5 mg/kg for apple was recommended for withdrawal by the 1994 JMPR

The international estimated short-term intake (IESTI) for phosalone was calculated for the commodities for which maximum residue levels and STMRs were estimated and for which consumption data were available. The results are shown in Annex IV of the 1999 JMPR Report. The IESTI varied from 0 to 0.034 mg/kg bw for the general population and from 0 to 0.118 mg/kg bw for children. As no acute reference dose was established, the acute risk assessment for phosalone was not finalized.

DIETARY RISK ASSESSMENT

Chronic intake

Six STMRs were estimated for phosalone. There were consumption data for the 5 main commodities which were used for the dietary intake calculation. The results are shown in Annex III.

The International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on estimated STMRs, were in the range of 0-4% of ADI. The Meeting concluded that the intake of residues of phosalone from uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The international estimated short-term intake (IESTI) for phosalone was calculated for the commodities for which maximum residue levels and STMRs were estimated and for which consumption data were available. The results are shown in Annex IV. The IESTI varied from 0 to 0.034 mg/kg bw for the general population and from 0 to 0.118 mg/kg bw for children. As no acute reference dose was established, the acute risk assessment for phosalone was not finalized.

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PYRIPROXYFEN (200)

IDENTITY

ISO common name: pyriproxyfen (draft E-ISO)

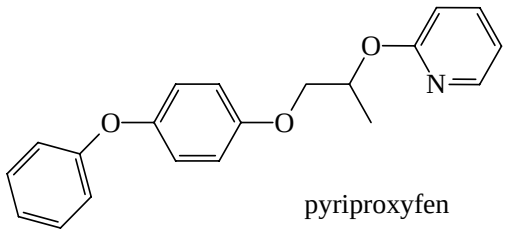
BSI name: pyriproxyfen

Chemical name
IUPAC: 4-phenoxyphenyl (*RS*)-2-(2-pyridyloxy)propyl ether
CA: 2-[1-methyl-2-(4-phenoxyphenoxy)ethoxy]pyridine

CAS No.: 95737-68-1 (unstated stereochemistry)

Synonyms: Company code numbers: S-31183, S-71639
Trade names: Admiral, Atominal, Juvinal, Knack, Nemesis, Prempt, Tiger

Structural formula:



pyriproxyfen

Molecular formula: $C_{20}H_{19}NO_3$

Molecular weight: 321.37

Physical and chemical properties

Pure active ingredient

Appearance: white odourless solid.

Vapour pressure: $<1.0 \times 10^{-7}$ mm Hg ($<1.3 \times 10^{-5}$ Pa) at 22.8°C. Vapour pressure was measured by the gas saturation procedure, but test material was not detected in the trapping tubes.

Melting point: 48.0-50.0°C

Octanol/water partition coefficient: $P_{ow} = 2.36 \times 10^5$ (log P = 5.37) at 25 ± 1°C.

Solubility:

water	0.367 ± 0.004 mg/l at 25 ± 1°C.
acetone	>150 g/100 g at 20°C
acetonitrile	>150 g/100 g at 20°C
hexane	6.97 (SD 0.460) g/100 g at 20°C
methanol	5.56 (SD 0.181) g/100 g at 20°C
methylene chloride	>150 g/100 g at 20°C

n-octanol	6.85 (SD 0.894) g/100 g at 20°C

Hydrolysis:

pyriproxyfen was stable in aqueous buffers in the dark at pH 4.0, 7.0 and 9.0 at 50°C and at pH 5.0, 7.0 and 9.0 at 25°C. Takahashi *et al.* (1989a,b) dissolved [*phenyl*-^{14}C]pyriproxyfen and [*pyridyl*-^{14}C]pyriproxyfen in sterile aqueous buffer solutions with 1% acetonitrile as co-solvent at 0.1 mg/l and analysed the solutions at intervals during 7 days at 50°C and 30 days at 25°C. No decrease of pyriproxyfen could be detected after 7 days at 50°C. Calculated half-lives were more than 200 days.

Technical material

Purity: minimum 95.0%

Stability: technical grade material stored at ambient temperature (19 - 35°C) for one year showed no change when analysed by HPLC.

Technical grade pyriproxyfen was also tested for stability when exposed to iron, elevated temperatures and sunlight. There was no degradation when the technical grade as a 1% solution containing either 0.1% ferric chloride hexahydrate or 0.025% iron powder was stored for 14 days at 20°C, or the product was held in a sealed bottle at 54°C for 14 days or exposed to sunlight in a transparent glass ampoule for 14 days.

METABOLISM AND ENVIRONMENTAL FATE

Studies of metabolic and environmental fate identified the compounds shown in Figure 1 and their conjugates.

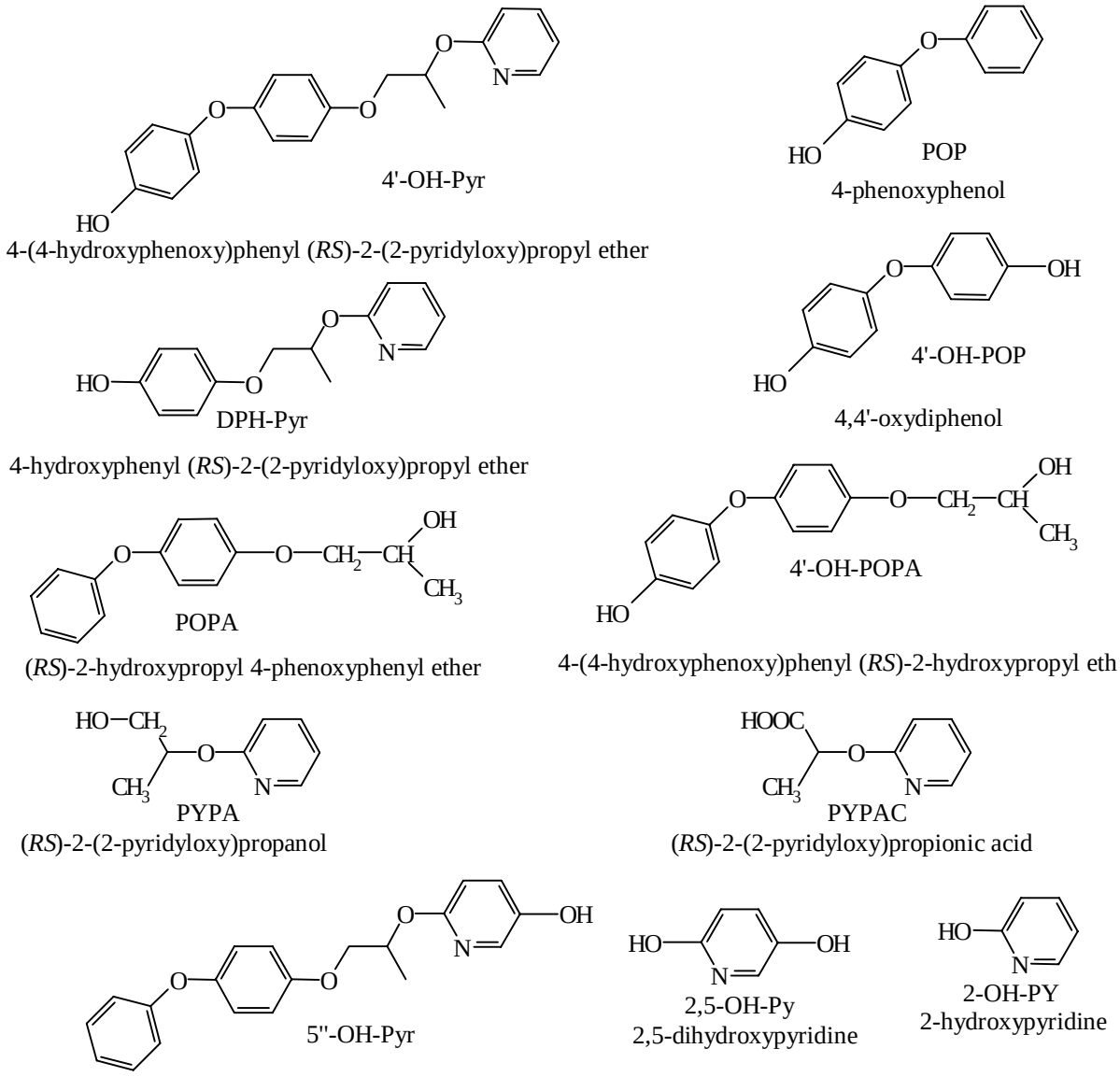
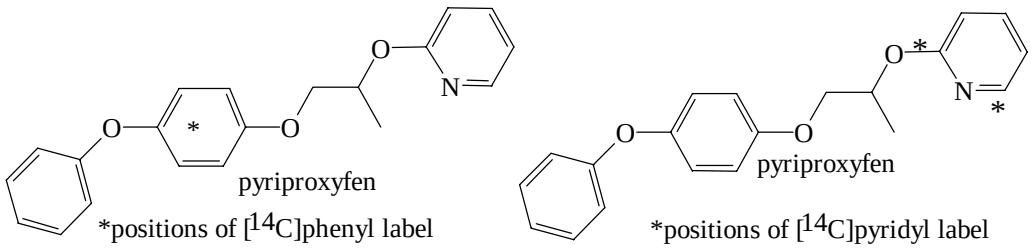


Figure 1. Structures, names and abbreviations of metabolites and degradation products found in studies of metabolism and environmental fate.

For the studies of metabolism and environmental fate pyriproxyfen was labelled either uniformly in the proximal ring of the phenoxyphenyl moiety or in positions 2 and 6 of the pyridine ring.



Animal metabolism

The Meeting received information on the metabolism of pyriproxyfen in rats, lactating goats and laying hens.

Isobe *et al.* (1988a) administered a single oral dose of [*phenyl*-^{14}C]pyriproxyfen to rats at 2 mg/kg bw (low dose) and 1000 mg/kg bw (high dose). Rats were also dosed orally with unlabelled pyriproxyfen at 2 mg/kg bw/day for 14 consecutive days followed by a single oral dose of labelled pyriproxyfen at the same rate. ^{14}C excretion was rapid, accounting for 88-96% in 2 days and 92-98% within 7 days. ^{14}C levels were higher in the fat than in other tissues. The main metabolite identified in the faeces was 4'-OH-Pyr, accounting for 25-54% of the dose; pyriproxyfen in the faeces accounted for 7-37% of the dose.

Isobe *et al.* (1988b) examined the distribution of ^{14}C in the tissues from the rats administered the single oral dose of 2 mg/kg bw of [*phenyl*-^{14}C]pyriproxyfen. Rats were killed for tissue collection 2, 4, 8, 12, 24, 48 and 72 hours after dosing. The radiolabel levels were higher in the liver than in other tissues for the first 8 hours after dosing, but higher in the fat than in other tissues after 72 hours. The radiolabel reached maximum levels in the liver, kidneys and muscle at 4-8 hours after dosing, and in fat at 12-24 hours. The highest levels of metabolites were of 4'-OH-Pyr sulfate and 5'',4'-OH-Pyr sulfate in the liver (Table 1). Yoshino (1993a) examined the distribution of ^{14}C in the tissues from the rats receiving the high dose (1000 mg/kg bw). Initially ^{14}C levels were higher in the liver than in other tissues but after 24 hours the levels were highest in the fat. The times to reach a maximum in each tissue were muscle and liver 2-8 h, kidneys 4-8 h and fat 12-24 h. The estimated biological half-life of ^{14}C in the fat was 36 hours. The metabolism studies on rats have subsequently been published (Matsunaga *et al.*, 1995).

Table 1. Maximum levels of ^{14}C expressed as pyriproxyfen associated with identified compounds in kidneys and liver of rats dosed orally with 2 mg/kg bw of [*phenyl*-^{14}C]pyriproxyfen, and time after dosing to reach maximum (Isobe *et al.*, 1988b).

Compound	Kidneys		Liver	
	max. ng/g	time, h	max, ng/g	time, h
Pyriproxyfen	39	2-4	63	2
4'-OH-Pyr	12	4	340	4-8
4'-OH-Pyr sulfate	80	4-8	770	2-8
4'-OH-POPA			15	8
4'-OH-POPA sulfate	34	8	160	8
5'',4'-OH-Pyr			21	8
5'',4'-OH-Pyr sulfate	153	4-8	735	8
4'-OH-POP sulfate	50	8	88	8

Yoshino (1993b) administered a single oral dose of [*pyridyl*-^{14}C]pyriproxyfen to rats at 2 mg/kg bw (low dose) and 1000 mg/kg bw (high dose). Excretion of ^{14}C accounted for 89-93% in 2 days and 92-99% within 7 days. ^{14}C levels were higher in the fat than in other tissues. The main metabolite identified in the faeces was 4'-OH-Pyr, accounting for 23-47% of the dose; pyriproxyfen accounted for 21-35%.

The rates of excretion and metabolic pathways of pyriproxyfen in rats and mice were shown to be similar (Yoshino *et al.*, 1995).

Studies of the metabolism of [*phenyl*-^{14}C] and [*pyridyl*-^{14}C] pyriproxyfen in lactating goats and laying hens were reported. A subsequent study of freezer storage stability (Green, 1997) showed

that pyriproxyfen and its metabolites in some animal substrates had limited storage stability at –20ºC. No data were available on the storage stability in milk or eggs. Samples of goat and chicken tissues, milk and eggs were generally extracted 60-90 days after collection in the four studies. Pyriproxyfen could have decreased by 35-45% in this time, 4'-OH-Pyr by less than 30%, 2,5-OH-Py by 60-70%. The studies should be interpreted in the light of the stability during freezer storage.

Residues in tissues, milk and excreta were measured in two lactating dairy goats, each weighing 51-57 kg, dosed orally for 5 consecutive days by capsule with 20 mg [*phenyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996a). The feed intake was 1.43-2.17 kg/animal/day. The two goats produced averages of 800 and 3200 g milk per day. Milk and excreta were collected throughout, and the animals were slaughtered 6 hours after the final dose for tissue collection (rear leg and loin muscle, omental and perirenal fat, liver, kidneys, heart and blood). The identified residues in the milk and tissues are shown in Tables 2 and 3.

Most of the radiolabel was accounted for by the faeces (58%), urine (17-18%) and GI tract (24%). Milk accounted for 0.29% and 0.79% of the dose in the two animals, while the livers contained 0.45% and 0.29%.

Pyriproxyfen was a minor component of the residue in the milk, accounting for 5-15% of the ^{14}C. The main residue was 4'-OH-Pyr sulfate accounting for about 50%, while POP sulfate, 4'-OH-POP sulfate and DPH-Pyr each accounted for between 5 and 10% of the total ^{14}C.

Pyriproxyfen was the major component in the fat, accounting for 50-79% of the ^{14}C. The residues in omental and perirenal fat were qualitatively and quantitatively similar. Pyriproxyfen was also the main residue component in muscle but the levels were very low. It was a very minor component of the residue in both kidneys and liver, accounting for 1-4% of the ^{14}C. The main residue in the kidneys was POP sulfate; 4'-OH-Pyr sulfate, 5''-OH-Pyr sulfate and 4'-OH-POP each exceeded 5% of the ^{14}C. The total residue level was higher in the liver than in other tissues; the main compounds were 4'-OH-Pyr sulfate, POPA, 4'-OH-Pyr and 4'-OH-POPA. The heart contained 0.035 and the blood 0.039 mg/kg of ^{14}C expressed as pyriproxyfen.

Table 2. Pyriproxyfen and identified metabolites in the milk of goats dosed orally for 5 consecutive days by capsule with [*phenyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996a). Residue levels are ^{14}C expressed as pyriproxyfen, mg/kg.

Compound	Day 2 milk				Day 4 milk			
	Goat A		Goat B		Goat A		Goat B	
	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C
pyriproxyfen	0.005	5.4	0.009	15	0.005	5.7	0.006	10
4'-OH-Pyr sulfate	0.044	50	0.025	45	0.049	51	0.028	49
4'-OH-Pyr	0.001	0.88	0.002	3.0	0.002	1.9	0.001	1.5
POP sulfate	0.009	10	0.005	9.0	0.010	10	0.006	9.7
4'-OH-POP sulfate	0.007	8.2	0.004	7.4	0.008	8.3	0.005	7.9
4'-OH-POPA sulfate	0.002	2.8	0.001	2.5	0.003	2.9	0.002	2.7
DPH-Pyr	0.007	8.1	0.004	7.2	0.008	8.2	0.004	7.8
TOTAL	0.090	100	0.060	100	0.096	100	0.058	100

Table 3. Pyriproxyfen and identified metabolites in the tissues of goats dosed orally for 5 consecutive days by capsule with [*phenyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996a). The residues in the 2 goats are shown separately.

Compound	^{14}C as pyriproxyfen, mg/kg					
	Kidneys	Liver	Loin muscle	Leg muscle[1]	Omental fat	Perirenal fat
pyriproxyfen	0.003 0.003	0.010 0.012	0.007 0.008	0.004	0.014 0.043	0.023 0.050
4'-OH-Pyr sulfate	0.052 0.029	0.121 0.078	0.002 0.002	0.001	0.001 0.002	0.001 0.002
4'-OH-Pyr	0.001 -	0.068 0.017	0.002 0.002	<0.001	0.007 0.004	0.008 0.003
5''-OH-Pyr		0.027 0.006				
5''-OH-Pyr sulfate	0.040 0.023	0.004 0.015				
POP sulfate	0.093 0.057					
POP	0.002 0.002	0.017 0.009	0.001 0.001	<0.001	0.001 0.001	0.001 0.001
4'-OH-POP	0.024 0.014		0.001 0.001	<0.001	<0.001 0.001	<0.001 0.001
4'-OH-POP sulfate	0.003 0.003					
POPA	0.008 0.004	0.076 0.039				
4'-OH-POPA	0.007 0.004	0.051 0.026				
DPH-Pyr	0.005 0.003	0.032 0.016				
TOTAL[2]	0.262 0.162	0.492 0.288	0.021 0.019	0.010	0.029 0.054	0.038 0.050

[1]Components of residue in leg muscle of goat B were not determined because total residue was <0.001 mg/kg
[2]Total residue measured by combustion analysis

Two other lactating dairy goats, each weighing 39-47 kg, were dosed orally daily for 5 consecutive days by capsule with 14.9 mg [*pyridyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996b). The feed intake was 1.09-1.77 kg/animal/day. The goats produced averages of 1270 and 1410 g milk per day. Milk and excreta were collected throughout, and the animals were slaughtered 6 hours after the final dose for tissue collection as before.

Most of the ^{14}C (62-70%) was excreted in the faeces and urine with about 31% in the gastrointestinal tract and contents. Less than 2% was distributed in the milk and tissues: 0.44% and 0.84% in the milk, 0.46% and 0.81% in the liver, 0.04% and 0.06% in the kidneys, 0.02 and 0.03% in muscle, 0.05% and 0.05% in fat. The residues in the milk and tissues are shown in Tables 4 and 5. Heart samples contained 0.029-0.039 and blood 0.038-0.041 mg/kg ^{14}C expressed as pyriproxyfen, representing 0.01% and <0.01% of the dose respectively. The administered ^{14}C was quantitatively recovered (95-102%).

Pyriproxyfen was a minor component of the residue in the milk accounting for 3.2-5.6% of the ^{14}C. The major residues were 4'-OH-Pyr sulfate (29-42%) and 2,5-OH-Py conjugate(s) (19-30%).

Pyriproxyfen was the main residue in fat, with essentially the same levels in the omental and perirenal fat, and was generally the major identified compound in muscle with the metabolites 4'-OH-Pyr sulfate, 2-OH-PY and PYPA conjugate(s) contributing 6-15% of the residue. The levels of pyriproxyfen were less than 10% of its levels in the fat, as would be expected for a fat-soluble compound.

Pyriproxyfen was a very minor part of the residue in the liver and kidneys (between about 0.3 and 1.4% of the total ^{14}C). 4'-OH-Pyr sulfate was the major identified component (22-39% in the kidneys and 7-20% in the liver), with 2,5-OH-Py and PYPA conjugates contributing about 7-13%. The total residues in the liver and kidneys were much higher than in the other tissues. About half the ^{14}C in the liver was unextractable. This was examined further by enzyme and acid hydrolysis but none of the known or expected metabolites were released. The chromatographic behaviour of the released ^{14}C suggested that it had been incorporated into natural products such as proteins or polysaccharides.

Table 4. Pyriproxyfen and identified metabolites in the milk of goats dosed orally for 5 consecutive days by capsule with [*pyridyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996b). Residue levels are ^{14}C expressed as pyriproxyfen, mg/kg.

Compound	Day 2 milk				Day 4 milk			
	Goat A		Goat B		Goat A		Goat B	
	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C	mg/kg	% of total ^{14}C
pyriproxyfen	0.003	4.2	0.003	3.2	0.004	5.6	0.003	3.0
4'-OH-Pyr sulfate	0.028	42	0.037	35	0.020	29	0.041	35
4'-OH-Pyr	0.001	0.76	<0.001	0.21	<0.001	0.4	<0.001	0.05
2,5-OH-Py conjugate	0.013	19	0.033	30	0.019	27	0.033	29
DPH-Pyr	0.004	6.4	0.006	5.5	0.003	4.5	0.006	5.6
TOTAL	0.063	100	0.111	100	0.071	100	0.121	100

Table 5. Pyriproxyfen and identified metabolites in the tissues of goats dosed orally for 5 consecutive days by capsule with [*pyridyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996b). The residues in the 2 goats are shown separately.

Compound	^{14}C as pyriproxyfen, mg/kg					
	Kidneys	Liver	Loin muscle	Leg muscle	Omental fat	Perirenal fat
pyriproxyfen	0.001 0.001	0.006 0.004	0.003 0.001	0.003 0.003	0.039 0.033	0.033 0.033
4'-OH-Pyr sulfate	0.088 0.065	0.085 0.060	0.001 0.002	0.001 0.002	0.001 0.001	0.002 0.002
4'-OH-Pyr	0.002 0.002	0.016 0.018	<0.001 0.001	<0.001 0.001	0.008 0.004	0.007 0.003
5"-OH-Pyr	0.001 0.001	0.009 0.011				
PYPA conjugate	0.022 0.039					
2,5-OH-Py conjugate	0.017 0.030	0.031 0.058				
PYPAC	0.005 0.009		<0.001 <0.001	<0.001 -		
PYPA conjugate		0.027 0.049	0.001 0.001	0.001 0.002		
2-OH-PY			0.002 0.001	0.002 -		
2,5-OH-Py			- <0.001			
TOTAL [1]	0.226 0.290	0.433 0.829	0.012 0.015	0.015 0.020	0.061 0.045	0.069 0.049

[1] Total residue measured by combustion analysis

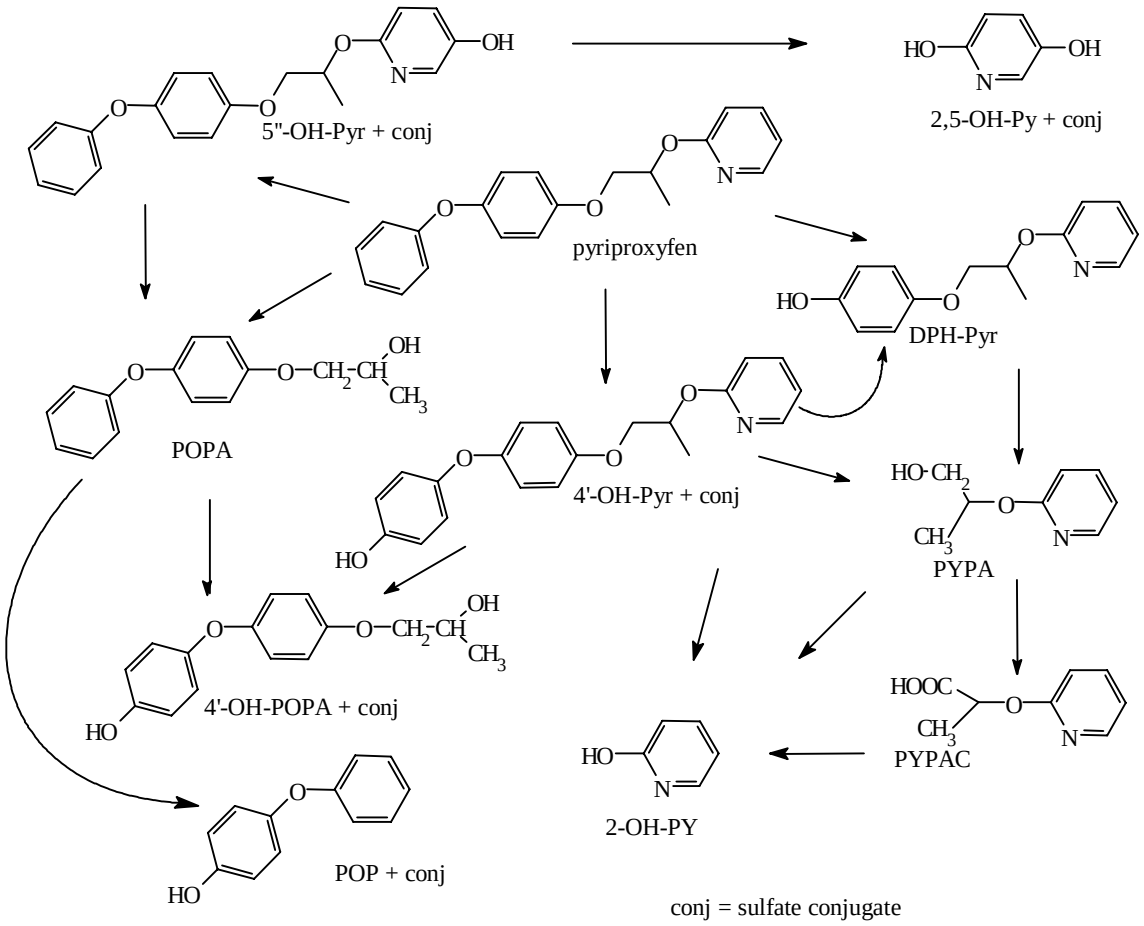


Figure 2. Metabolic fate of pyriproxyfen in lactating goats.

Ten Leghorn laying hens, each bird weighing 1.48-1.77 kg, were dosed orally daily for 8 consecutive days by capsule with 1.26 mg [*phenyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996c). The feed intake was 108-139 g/bird/day. Eggs and excreta were collected throughout, and birds were slaughtered within 4 hours of the final dose for tissue collection.

Approximately 96% of the ^{14}C was accounted for, with 89% in the excreta including the cage wash, 4.3% in the GI tract and contents, 2.6% in other tissues and 0.18% in eggs. The residue level in the gizzard was higher than in other tissues. The major identified residue in the excreta was 4'-OH-Pyr. The distribution of the radiolabel in the tissues and eggs is shown in Table 6 and the distribution of the identified compounds in Table 7.

Residue levels were very low in the egg white and apparently reached a plateau in the yolk in 6 days. Pyriproxyfen represented 55% of the ^{14}C in 7-day yolks with 4'-OH-Pyr accounting for 21% and 4'-OH-Pyr sulfate for 10%. Minor metabolites identified in egg yolk included DPH-Pyr, 4'-OH-POP and 4'-OH-POPA. The residue levels in muscle were lower than in the other tissues; pyriproxyfen accounted for 56% and 77% of the residue in breast and thigh muscles respectively. Residues in the fat were much higher than in the muscle, suggesting a fat-soluble residue; pyriproxyfen constituted 94% and 71% of the residue in the abdominal fat and the skin with fat respectively, and the level of pyriproxyfen in abdominal fat was 4.6 times the level in skin with fat. Pyriproxyfen was a minor component of the residue in the liver, in which 4'-OH-Pyr sulfate was the major component, accounting for 40% of the ^{14}C.

Table 6. Distribution of ^{14}C in the tissues and eggs of laying hens dosed for 8 days with [*phenyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996c).

Sample	^{14}C as pyriproxyfen, mg/kg		^{14}C as % of dose
Muscle, breast	0.033		0.02
Muscle, thigh	0.085		0.06
Fat, abdominal	0.88		0.06
Fat, skin attached	0.21		0.03
Kidneys	0.86		0.13
Liver	0.75		0.39
Heart	0.23		0.02
Blood	0.17		0.36
Gizzard	3.91		1.23
GI tract	3.51		4.32
Reproductive organs	0.20		0.26
Eggs	yolk	white	0.18
day 1	0.016	0.001	
day 2	0.021	0.004	
day 4	0.16	0.004	
day 6	0.30	0.006	
day 7	0.23	0.003	

Table 7. Pyriproxyfen and identified metabolites in the tissues of laying hens dosed for 8 days with [*phenyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996c).

Compound	^{14}C as pyriproxyfen, mg/kg							
	Kidneys	Liver	Breast muscle	Thigh muscle	Abdominal fat	Skin with fat	Gizzard	Egg yolk
pyriproxyfen	0.057	0.046	0.014	0.069	0.79	0.17	1.8	0.13
4'-OH-Pyr sulfate	0.089	0.27	0.002	0.005		0.012	0.57	0.024
4'-OH-Pyr	0.012	0.029	0.001	0.003	0.031	0.009	0.035	0.049
POP sulfate		0.022				0.006		
POP					0.005			
4'-OH-POP	0.031			0.001	0.001		0.058	0.001
4'-OH-POP sulfate	0.073	0.044				0.003		
POPA		0.035			0.001	0.008	0.089	
4'-OH-POPA	0.022		0.001	0.001		0.006	0.059	0.002
4'-OH-POPA-sulfate	0.073	0.025						
DPH-Pyr	0.011	0.036	0.002	0.002	0.001		0.094	0.009
TOTAL [1]	0.75	0.68	0.025	0.090	0.84	0.24	4.4	0.24

[1] Sum of bound and extractable ^{14}C

Ten Leghorn laying hens, each weighing 1.31-1.78 kg were similarly dosed for 8 days with 1.26 mg [*pyridyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed or a mean daily dose of 0.78 mg/kg bw (Panthani *et al.*, 1996d). The average feed intake was 110-138 g/bird/day. Samples were taken as before.

Approximately 88% of the ^{14}C was accounted for, with 84% of the dose in the excreta including the cage wash, 1.6% in the GI tract and contents, 2.3% in other tissues and 0.29% in eggs. The residue level in the gizzard was higher than in other tissues. The major identified residues in the excreta were PYPAC and 4'-OH-Pyr. The distribution of ^{14}C in the tissues and eggs is shown in Table 8 and that of the identified compounds in Table 9.

Residue levels were low in the egg white; residues in the yolk had almost reached a plateau by day 7. Pyriproxyfen accounted for 41 of the ^{14}C in 7-day yolks with 4'-OH-Pyr sulfate accounting

for 29%. Residue levels in muscle were lower than in the other tissues; pyriproxyfen accounted for 30% and 54% of the residue in muscle. Residues in the fat were much higher, with pyriproxyfen amounting to 87 and 62% of the residue in the abdominal fat and the skin with fat; the level of pyriproxyfen in the abdominal fat was 7 times its level in the skin with fat. Pyriproxyfen was a minor component (0.44%) of the residue in the liver, in which 4'-OH-Pyr sulfate was the major component accounting for 26% of the ^{14}C.

Table 8. Distribution of ^{14}C in the tissues and eggs of laying hens dosed for 8 days with [*pyridyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996d).

Tissue	^{14}C as pyriproxyfen, mg/kg		^{14}C as % of dose
Muscle, breast	0.054		0.04
Muscle, thigh	0.11		0.07
Fat, abdominal	0.93		0.03
Fat, skin attached	0.27		0.03
Kidneys	0.80		0.12
Liver	0.69		0.34
Heart	0.27		0.03
Blood	0.28		0.60
Gizzard	1.8		0.60
GI tract	1.14		1.6
Reproductive organs	0.34		0.45
Eggs	yolk	white	0.29
Day 1	0.002	0.002	
Day 2	0.012	0.013	
Day 4	0.19	0.017	
Day 6	0.38	0.020	
Day 7	0.41	0.019	

Table 9. Pyriproxyfen and identified metabolites in the tissues of laying hens dosed for 8 days with [*pyridyl*-^{14}C]pyriproxyfen equivalent to 10 ppm pyriproxyfen in the feed (Panthani *et al.*, 1996d).

Compound	^{14}C as pyriproxyfen, mg/kg							
	Kidneys	Liver	Breast muscle	Thigh muscle	Abdominal fat	Skin with fat	Gizzard	Egg yolk (day 7)
pyriproxyfen	0.041	0.011	0.013	0.047	0.92	0.13	0.48	0.17
4'-OH-Pyr sulfate	0.057	0.18	0.003	0.002		0.023	0.17	0.12
4'-OH-Pyr	0.006	0.015	0.001	0.001	0.030	0.005	0.043	0.012
5"-OH-Pyr		0.003						
5"-OH-Pyr sulfate		0.011						
PYPA							0.010	
DPH-Pyr	0.011		0.001	0.002	0.009			0.013
2-OH-PY	0.069	0.087	0.013	0.014		0.013	0.021	0.007
PYPAC	0.060	0.025	0.007	0.006	0.001	0.012	0.008	
TOTAL [1]	0.75	0.68	0.044	0.087	1.06	0.21	0.95	0.41

[1] Sum of bound and extractable ^{14}C

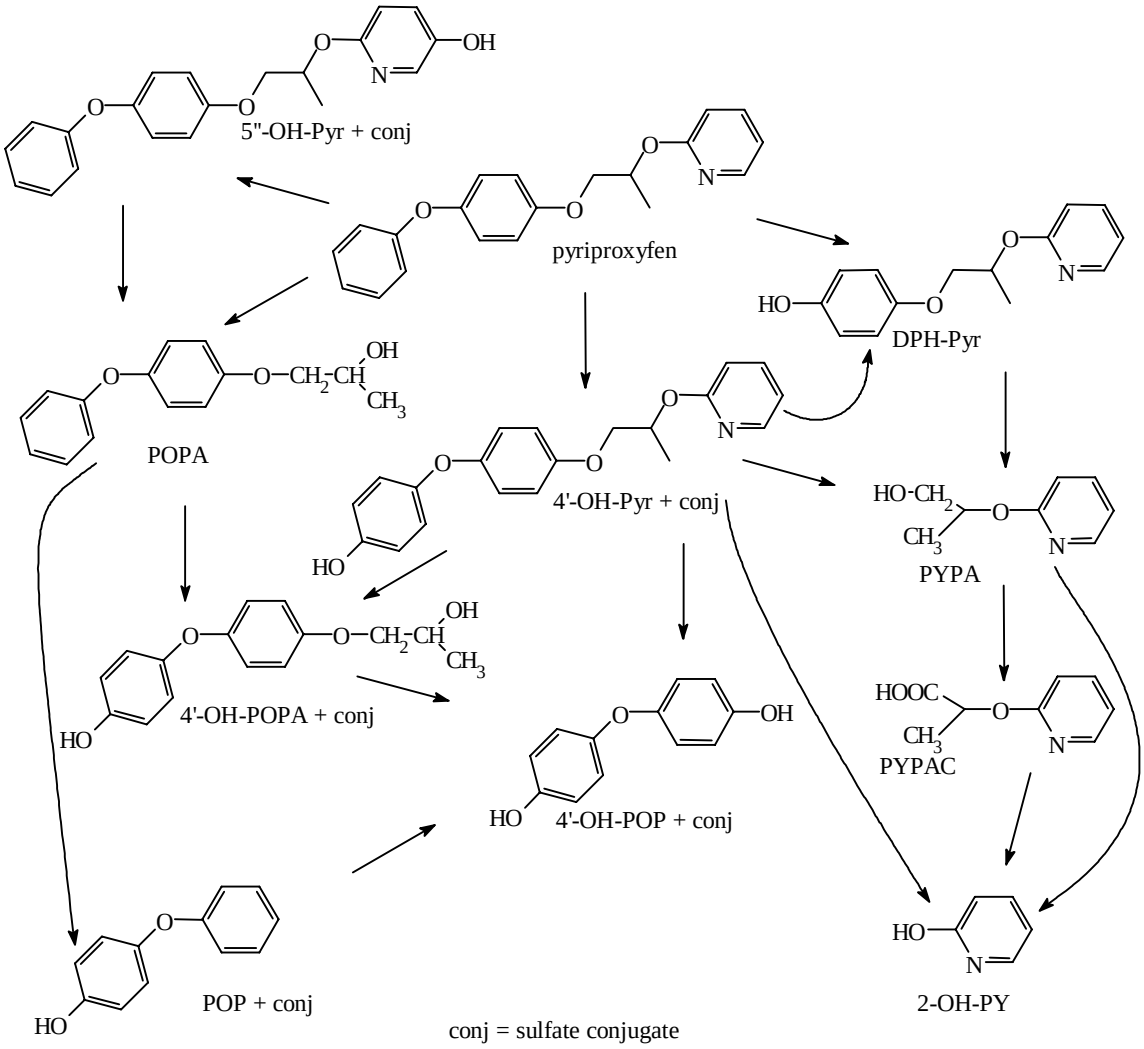


Figure 3. Metabolic fate of pyriproxyfen in laying hens

Plant metabolism

The Meeting received information on the metabolism of pyriproxyfen in apples, tomatoes and cotton.

Panthani and Walsh (1996) treated apple trees three times (soon after petal fall and at 60 and 40 days before harvest) with phenyl- and pyridyl-labelled pyriproxyfen at 150 g/ha. The residues found in mature apples are shown in Table 10.

A surface wash with acetonitrile removed 1.5-2.6% of the total residue. The washed apples were homogenized and centrifuged to produce juice and pomace. Juice fractions contained 6-14% of the ^{14}C and pomace 84-92%. About 70% of the ^{14}C in the pomace was extractable with methanol, with 12-15% unextractable after acid treatment and other extractions. Pyriproxyfen was not detectable (<0.001 mg/kg) in the juice, where the main identified residue was PYPA which accounted for 25% of the ^{14}C in the juice and 3.2% of that in the apples. Pyriproxyfen accounted for most of the ^{14}C in the pomace and for 52 and 54% of the total ^{14}C in the whole apples.

Table 10. Residues in mature apples from trees treated three times with phenyl- or pyridyl-labelled [^{14}C]pyriproxyfen at 150 g/ha and harvested 40 days after the final application (Panthani and Walsh, 1996).

Residue	^{14}C as pyriproxyfen, mg/kg	
	phenyl label	pyridyl label
Extractable [1]	0.16	0.16
Pyriproxyfen	0.097	0.101
4'-OH-Pyr [2]	0.021	0.017
PYPA [3]		0.012
DPH-Pyr [3]	0.006	0.003
POPA [3]	0.004	
4'-OH-POPA [4]	0.004	
POP [3]	0.002	
4'-OH-POP [4]	0.001	
5''-OH-Pyr [4]	0.001	<0.001
PYPAC [2]		0.003
Unextractable	0.028	0.023

[1] Including surface wash
[2] Free
[3] Sum of free and conjugated
[4] Conjugated

Panthani and DiFrancesco (1997) treated tomato plants three times (35, 21 and 7 days before harvest) with phenyl- or pyridyl-labelled pyriproxyfen at 150 g/ha. The residues in the tomatoes are shown in Table 11. A surface wash with acetonitrile removed 1.8-3.3% of the total residue. The washed tomatoes were homogenized and centrifuged to produce juice and pomace. Juice fractions contained 14% and 33% of the ^{14}C from the phenyl and pyridyl label respectively, and the pomace 82% and 65%. Approximately 92-95% of the ^{14}C in pomace was extractable with acetonitrile/water.

Pyriproxyfen was not detectable in the tomato juice, where the main identified residues were PYPA (free 0.007 mg/kg, conjugated 0.018 mg/kg), PYPAC (free 0.010 mg/kg, conjugated 0.008 mg/kg) and 2-OH-PY (conjugated 0.013 mg/kg) accounting for 29%, 21% and 15% of the ^{14}C respectively. Pyriproxyfen accounted for most of the residue in the pomace and for 68% and 50% of the total phenyl and pyridyl labels respectively in the whole tomatoes.

Table 11. Residues in tomatoes from plants treated three times with phenyl- or pyridyl-labelled [^{14}C]pyriproxyfen at 150g/ha and harvested 7 days after the final application (Panthani and DiFrancesco, 1997).

Residue	^{14}C as pyriproxyfen in tomatoes, mg/kg	
	phenyl label	pyridyl label
Extractable [1]	0.34	0.25
Pyriproxyfen	0.24	0.13
4'-OH-Pyr	0.020	0.012
PYPAC [2]		0.021
PYPA [3]		0.029
2-OH-PY [3]		0.013
4'-OH-POPA [2]	0.009	
DPH-Pyr [3]	0.008	0.005
4'-OH-POP [2]	0.007	
Unextractable	0.016	0.014

[1] including surface wash
[2] sum of free and conjugated
[3] conjugated

Panthani *et al.* (1996e) treated field cotton plants 43 and 28 days before harvest at 150 g/ha, and glasshouse plants at 590 g/ha 42 and 28 days before harvest, with phenyl- or pyridyl-labelled pyriproxyfen. The higher rate was to provide a source of material for the identification of metabolites. The residues in the cotton seed and gin trash are shown in Table 12.

Pyriproxyfen was metabolized to polar compounds in the plants, with most of the residue remaining in the foliage. Pyriproxyfen was the main residue component in the gin trash. Residues were much lower in the seed than in the gin trash, suggesting little if any translocation of residue from leaf to seed. Pyriproxyfen constituted only 3.9% and 0.6% of the residue in the seed, where the main identified residue was PYPAC in free and conjugated forms. Much of the residue in the cotton seed (49 and 55%) was unextractable; about half of this was associated with the protein fraction and the remainder with carbohydrate and lignin.

Table 12. Residues in cotton seed and gin trash from cotton plants treated twice with phenyl- or pyridyl-labelled [^{14}C]pyriproxyfen at 150g/ha and harvested 28 days after the second application (Panthani *et al.*, 1996e).

Residue	^{14}C as pyriproxyfen, mg/kg			
	Cotton seed		Gin trash	
	phenyl label	pyridyl label	phenyl label	pyridyl label
Extractable	0.016	0.069	1.4	3.6
Pyriproxyfen	0.0012 [3]	0.0009 [4]	0.76	1.5
4'-OH-Pyr	0.0001	0.0001	0.13	0.27
DPH-Pyr [1]			0.13	0.32
OH-pyriproxyfen [2]			0.032	0.17
PYPAC [1]		0.020		0.20
PYPA [1]		0.0059		0.093
POPA			0.044	
4'-OH-POPA			0.035	
POP			0.019	
Unextractable	0.015	0.084	0.39	0.81

[1] sum of free and conjugated
[2] sugar sulfate conjugate of pyriproxyfen hydroxylated in the pyridine ring
[3] 28% in the surface rinse
[4] 35% in the surface rinse

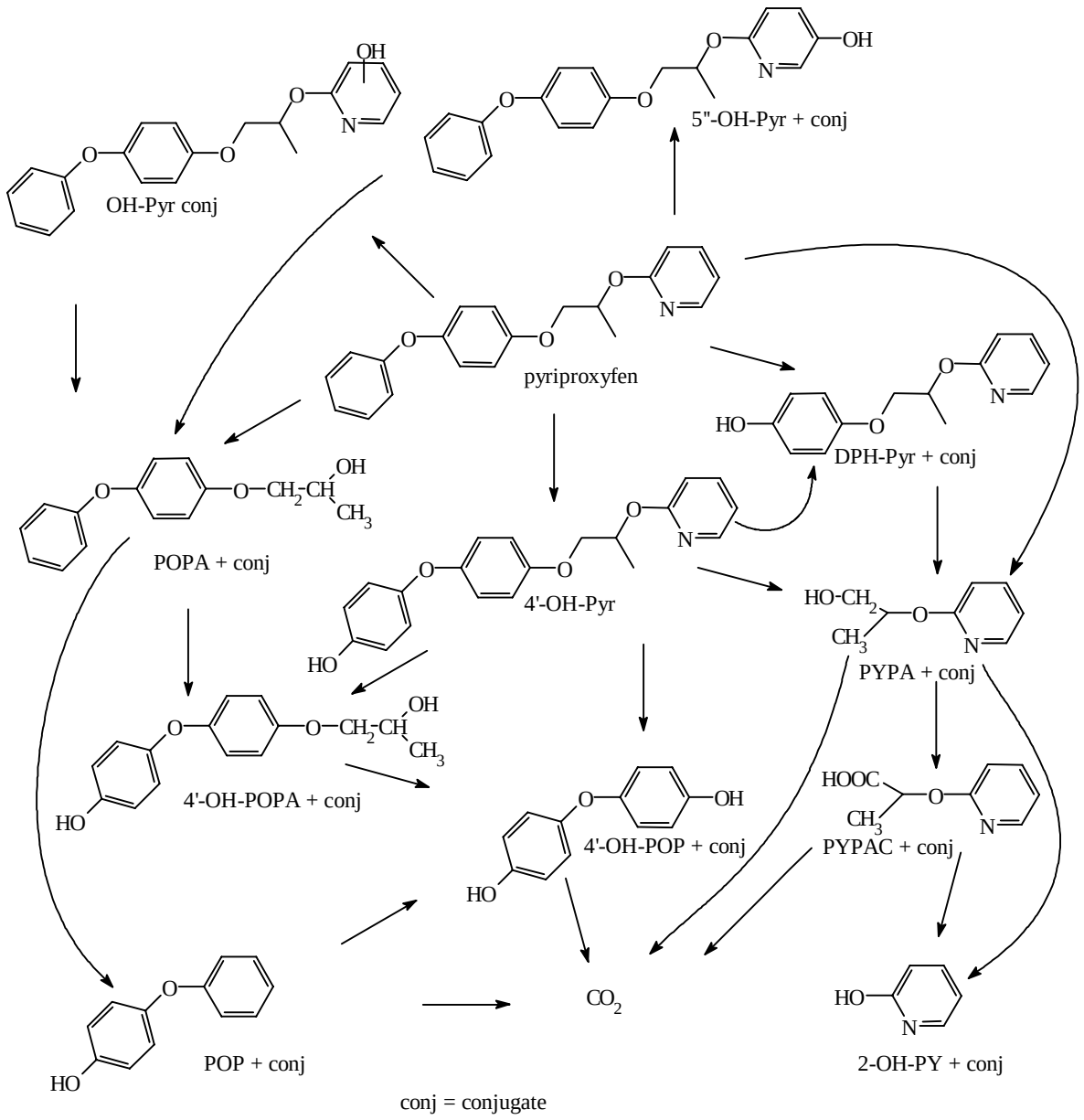


Figure 4. Metabolic fate of pyriproxyfen in apples, tomatoes and cotton.

Environmental fate in soil

Kouno *et al.* (1990a) incubated [*phenyl*-^{14}C]pyriproxyfen and [*pyridyl*-^{14}C]pyriproxyfen in a sandy clay loam soil (73% sand, 8% silt, 19% clay, 2.4% organic content, pH 5.7) at 0.5 mg/kg under aerobic conditions at 25°C in the dark for 30 days. The recovery of ^{14}C, including volatiles, was in the range 91-103%. The residues are shown in Table 13. Pyriproxyfen disappeared rapidly in the initial stages, but later more slowly: its estimated half-life after the first 7 days was 28 days. The estimated mineralization half-lives were 68 and 139 days for the pyridyl and phenyl labels respectively, with an indication that mineralization was slower after longer intervals. The main identified residue was 4'-OH-Pyr. Other minor products were PYPAC, DPH-Pyr and 4'-OH-POPA. A substantial part of the ^{14}C quickly became bound in the soil organic matter.

Table 13. Residues found during aerobic degradation of phenyl- and pyridyl-labelled pyriproxyfen in a sandy clay loam soil (Kouno *et al.*, 1990a). The recorded results are means of two separate experiments with each label.

Days	^{14}C, % of applied								
	pyriproxyfen		CO_2		4'-OH-Pyr [1]		PYPAC [1]	Bound	
	phenyl label	pyridyl label	phenyl label	pyridyl label	phenyl label	pyridyl label	pyridyl label	phenyl label	pyridyl
0	95	95						0.8	0.9
1	87	93			1.5	1.1		4.7	3.0
3	63	64	4.1	3.6	2.5	3.7	1.0	20	17
7	45	46	8.3	12.6	2.8	4.2	0.7	36	31
14	38	36	11	18	2.6	3.2	0.9	42	38
30	25	25	17	28	2.7	2.7		46	34

[1] Additional amounts were identified in the fulvic acid fraction of the bound residues

Kouno *et al.* (1990b) carried out an identical experiment with sandy loam soil (54% sand, 36% silt, 10% clay, 0.8% organic content, pH 6.5) but continued the incubation for 91 days. The recovery of ^{14}C, including volatiles, was in the range 88-106%. The residues are shown in Table 14. The estimated half-lives of pyriproxyfen were 8.2 days during days 1-14 and 20 days during days 14-91. The rates for the phenyl and pyridyl labels were very similar. The estimated mineralization half-lives (calculated from the rates of $^{14}CO_2$ production) were 112 and 82 days for the phenyl and pyridyl labels respectively.

PYPAC was the main identified product, with the sum of free and bound PYPAC exceeding pyriproxyfen from day 28. 4'-OH-Pyr was a minor product, at its highest on day 1 and decreasing with estimated half-lives of 29 and 39 days for the phenyl and pyridyl labels respectively. Bound residues accounted for approximately 50% of the applied ^{14}C by day 28. Other identified products representing 0.1-0.2% of the applied ^{14}C were detected intermittently.

Table 14. Residues found during aerobic degradation of phenyl- and pyridyl-labelled pyriproxyfen in a sandy loam soil (Kouno *et al.*, 1990b). The recorded results are means of two separate experiments with each label.

Days	^{14}C, % of applied									
	pyriproxyfen		CO_2		4'-OH-Pyr		PYPAC free	PYPAC bound	Bound	
	phenyl label	pyridyl label	phenyl label	pyridyl label	phenyl label	pyridyl label	pyridyl label	pyridyl label	phenyl label	pyridyl label
0	94	96	0.0	0.0	0.3	0.3	0.0	0.0	2.1	2.0
1	77	84	1.9	0.2	0.9	0.8	1.1	0.0	9.5	9.4
3	66	70	5.8	1.6	0.9	0.7	2.5	3.7	19	18
7	49	51	11.2	5.1	0.7	0.6	3.7	6.2	25	27
14	27	29	19	10.9	0.5	0.5	6.3	7.6	40	37
28	8.7	13.0	30	24	0.4	0.4	5.4	9.5	52	50
59	3.0	3.6	38	46	0.2	0.2	2.8	3.3	50	45
91	1.5	2.3	43	50	0.1	0.2	1.7	2.8	51	40

Fathulla *et al.* (1994) incubated [*phenyl*-^{14}C] and [*pyridyl*-^{14}C]pyriproxyfen aerobically in a sandy loam soil (pH 7.6, organic matter 0.87%, clay 8.4%) at 0.6 mg/kg in the dark at 25°C for 6 months and measured the evolved CO_2 and the levels of pyriproxyfen and identifiable products. The recoveries of ^{14}C were in the range 94% to 108%. The results are shown in Tables 15 and 16.

Mineralization was slow with 13.9% of the ^{14}C from the phenyl label and 31.1% from the pyridyl label evolved as CO_2 after 180 and 189 days, equivalent to mineralization half-lives of 850 and 330 days. Pyriproxyfen disappeared quickly in the first 14 days with estimated initial half-lives of

6.3 and 9.1 days for the phenyl and pyridyl labels, but much more slowly between 2 and 6 months, with estimated half-lives of 120 and 77 days for the phenyl and pyridyl labels respectively.

Identified products were generally minor proportions of the residue; 4'-OH-Pyr and PYPAC reached their highest measured levels on day 14 and then decreased. The polar material, which accounted for 22-23% of the applied ^{14}C after 6 months, could not be identified but was characterized as a mixture of high-molecular-weight compounds, suggesting incorporation or binding to natural products.

Table 15. Aerobic degradation of [*phenyl*-^{14}C]pyriproxyfen incubated with sandy loam soil at 0.6 mg/kg in the dark at 25°C for 6 months (Fathulla *et al.*, 1994).

Days	^{14}C, % of applied				
	Pyriproxyfen	Polar material [1]	4'-OH-Pyr	DPH-Pyr	CO_2
0	104	nd	nd	nd	
1	100	nd	nd	nd	<0.1
3	87	5.8	nd	nd	0.1
7	47	10	2.2	nd	0.5
14	24	18	3.3	0.4	3.5
31	13	16	2.6	0.1	5.7
62	10.3	23	1.3	0.2	8.8
94	7.5	26	0.8	0.1	10.7
122	6.7	27	0.6	0.1	11.5
150	6.9	26	0.5	0.1	12.8
180	5.0	23	0.4	<0.1	13.9

[1] Material remaining at TLC origin

Table 16. Aerobic degradation of [*pyridyl*-^{14}C]pyriproxyfen incubated with sandy loam soil at 0.6 mg/kg in the dark at 25°C for 6 months (Fathulla *et al.*, 1994).

Day	^{14}C, % of applied					
	Pyriproxyfen	Polar material [1]	PYPAC	4'-OH-Pyr	DPH-Pyr	CO_2
0	102	nd	nd	nd	nd	
1	104	nd	nd	nd	nd	0.1
3	88	nd	1.0	5.3	nd	0.6
7	66	13.5	3.1	nd	nd	1.6
14	36	12.6	7.6	6.3	0.3	4.6
30	23	16	4.9	2.7	0.2	12.5
59	11.4	18	1.4	1.8	0.2	20
92	7.7	20	0.6	1.6	0.1	24
120	6.3	21	0.4	1.0	0.1	27
149	7.1	16	0.5	0.9	nd	29
189	4.5	22	0.3	0.9	nd	31

[1] Material remaining at TLC origin

Mikami *et al.* (1989) determined the leaching of [*phenyl*-^{14}C]pyriproxyfen freshly mixed at 1 mg/kg with a silt soil (43% sand, 47% silt, 10% clay, 7.6% organic matter, pH 7.0) and a sandy loam (72% sand, 17% silt, 11% clay, 0.9% organic matter, pH 7.2) and applied to 30 cm x 3 cm i.d. columns of the untreated soils. The columns were leached with water (360 ml) at 69 mm/day for 8 days. Most of the ^{14}C (89% for the silt soil and 84% for the sandy loam) still remained in the treated portion at the top of the soil columns, with 5% in the 0-5 cm untreated layer of both soils. Small amounts of ^{14}C were detected throughout the columns with 0.1% and 2.8% in the eluates from the silt and sandy loam respectively. Most of the extractable residue was pyriproxyfen (Table 17) with bound ^{14}C in the humin, humic acid and fulvic acid fractions. Small amounts of DPH-Pyr and 4'-OH-Pyr were identified in the extracted and fulvic acid fractions. Pyriproxyfen is unlikely to be leached and its degradation products become substantially bound in the soil organic matter.

Table 17. ^{14}C residues in two soil columns after leaching fresh [*phenyl*-^{14}C]pyriproxyfen for 8 days (Mikami *et al.*, 1989).

Residue	^{14}C, % of applied	
	Silt soil	Sandy loam soil
Extracted ^{14}C	31	43
pyriproxyfen	25	34
DPH-Pyr	0.9	0.7
4'-OH-Pyr	2.9	1.8
Bound ^{14}C	58	39
fulvic acid	14	9.4
DPH-Pyr	1.9	1.1
4'-OH-Pyr	0.7	0.5
humic acid	16	10.6
humin	28	19

Fathulla *et al.* (1993a) incubated [*phenyl*-^{14}C]pyriproxyfen and [*pyridyl*-^{14}C]pyriproxyfen with a sandy loam soil (pH 8.1, organic matter 0.79%, clay 23%) under aerobic conditions in the dark at 25°C for 14 days and used the treated soil after 9 days for leaching experiments. The composition of the residues during the incubation is shown in Tables 18 and 19. The half-life of pyriproxyfen was 7.5 and 9.5 days and the mineralization half-life was 170 and 140 days in the two systems.

Glass columns (5.1 cm i.d.) that could be separated into six 6 cm sections were used for the leaching experiments. A 3-cm layer of soil with aged residue was placed on top of the soil column and the column was leached with 1030 ml of 0.015N $CaCl_2$. In the experiment with the phenyl label 86% of the ^{14}C remained in the treated soil (top 3 cm), with 2.3% in section 2 (3-9 cm), 0.13-0.54% in the other sections and 1.0% in the leachate, giving a total recovery of 90%. Most of the residue consisted of pyriproxifen (26%) and bound material (44.5%). With the pyridyl label, 88.5% of the ^{14}C remained in the top 3 cm, with 1.4% in the 3-9 cm section, 0.13-0.44% in the other sections and 7.6% in the leachate: a total recovery of 98.6%. Most of the ^{14}C was associated with pyriproxyfen (35%) and bound residue (41%). PYPAC was the main residue in the leachate, 6.5 of the 7.6%. The leaching of pyriproxyfen is slight but PYPAC, constituting only a few per cent of the residue, is apparently mobile.

Table 18. Residues resulting from aerobic incubation at 25°C of [*phenyl*-^{14}C]pyriproxyfen with a sandy loam soil at 0.6 mg/kg (Fathulla, 1993a).

Days	Distribution of ^{14}C, % of applied.						
	Pyriproxyfen	Unidentified P1	DPH-Pyr	4'-OH-Pyr	Total unidentified	Unextractable	CO_2
0	95	0.09	0.10	0.19	1.9	3.0	0
2	71	0	0.64	6.3	4.7	8.0	0.27
4	64	0.72	1.9	8.2	4.8	20	1.1
7	44	0.78	1.6	5.3	9.4	29	2.6
9	39	0.54	1.4	5.1	7.7	37	3.5
9 [1]	41	0.34	1.8	4.4	8.5	41	3.5
11	31	1.4	2.0	5.5	8.9	42	4.3
14	26	0.77	1.5	3.6	8.3	48	5.3

[1] Beginning of leaching experiment

Table 19. Residues resulting from aerobic incubation at 25°C of [*pyridyl*-^{14}C]pyriproxyfen with a sandy loam soil at 0.6 mg/kg (Fathulla, 1993a).

Days	Distribution of ^{14}C, % of applied.						
	Pyriproxyfen	PYPAC	DPH-Pyr	4'-OH-Pyr	Total unidentified	Unextractable	CO_2
0	95	0.15	0.05	0.24	1.8	2.4	0
2	84	0.68	0.79	5.4	1.8	6.7	0.01
4	72	1.4	1.1	4.4	3.7	16	1.1
7	55	2.1	1.3	4.4	3.6	29	3.1
9	48	1.8	0.81	3.4	2.9	36	4.2
9 [1]	51	1.5	0.37	2.2	2.6	36	4.2
11	42	4.3	0.72	3.1	3.1	39	4.9
14	36	4.4	0.44	3.3	4.8	48	6.2

[1] Beginning of leaching experiment

Nambu *et al.* (1989) measured the adsorption and desorption of [*phenyl*-^{14}C]pyriproxyfen with 4 soils, a loam, clay loam, sandy loam and sand, after determining the water solubility to be 0.54 mg/l at 20°C. Adsorption and desorption measurements were made with 0.01 M $CaCl_2$ solutions of pyriproxyfen in equilibrium with the soils at 25°C in the dark (Table 20). K_{oc} values were calculated from the K_d and the percentage of organic carbon. The measured K_d and K_{oc} values suggest that pyriproxyfen is unlikely to be leached into ground-water. Cohen *et al.* (1984) interpreted K_d values below 1-5 and K_{oc} values below 300-500 as indicating potential leaching if other requirements, such as environmental persistence, are met.

Table 20. Properties and adsorption and desorption constants of pyriproxyfen for four soils (Nambu *et al.*, 1989).

Soil	Soil properties						Adsorption		Desorption	
	sand	silt	clay	organic matter	pH	CEC, meq/100 g	K_d	K_{oc}	K_d	K_{oc}
Loam	56%	30%	15%	8.2%	7.1	32	614	13000	755	16000
Clay loam	55%	26%	19%	1.9%	7.0	6.3	637	58000	925	84000
Sandy loam	72%	18%	11%	0.9%	7.2	2.8	142	27000	182	35000
Sand	98%	0.8%	1.5%	<0.1%	6.6	4.9	25	-	36	-

Fathulla *et al.* (1991) measured the adsorption and desorption of [*phenyl*-^{14}C]pyriproxyfen with 5 agricultural soils and a lake sediment. Pyriproxyfen at 1-50 ng/g dissolved in 10 ml aqueous 0.01M $Ca(NO_3)_2$ was added to 2 g of soil or sediment and shaken at 24.3°C for 2 hours. ^{14}C levels were measured in 7 ml of clear solution after centrifugation, and adsorption to the soil or sediment was calculated. To measure desorption, 7 ml aqueous 0.01M $Ca(NO_3)_2$ was added to the same tube with further shaking for 2 hours at 24.3°C. ^{14}C was measured in the clear solution after centrifugation and desorption was calculated. The results are shown in Table 21. Pyriproxyfen was soluble and stable at the concentrations tested. The recovery of ^{14}C ranged from 90% to 107% showing that losses by volatilization or adsorption to the containers were minimal. Pyriproxyfen was rated as essentially immobile and unlikely to be leached from most agricultural soils.

Table 21. Properties and adsorption and desorption constants of pyriproxyfen for a sediment and 5 agricultural soils (Fathulla *et al.*, 1991).

Soil	Soil properties						Adsorption		Desorption	
	sand	silt	clay	organic matter	pH	CEC, meq/100 g	K_d	K_{oc}	K_d	K_{oc}
Lake sediment	97%	1%	2%	0.4%	7.6	4	11.7	4980	10.0	4260
Sand	97%	1%	2%	0.3%	5.4	1.1	20.4	11600	25.1	14300
Sandy loam	60%	25%	15%	1.65%	8.0	9.7	126	12600	141	14100
Silt loam	29%	58%	13%	1.1%	7.0	13	174	26900	178	27500
Silty clay loam	7%	53%	49%	1.4%	7.8	27	282	34200	275	33400
Clay loam	21%	47%	32%	5.0%	7.0	21	324	11000	457	15500

Fathulla *et al.* (1995a,b) measured the adsorption and desorption of 4'-OH-Pyr and PYPAC on four agricultural soils and a lake sediment. In initial experiments, the solubility of 4'-OH-Pyr was measured as 1.1 µg/ml at 25°C and that of PYPAC as 89.1 mg/ml at .21.4°C.

[*Pyridyl*-^{14}C]4'-OH-Pyr at 25, 50, 250 and 500 ng/g dissolved in 10 ml aqueous 0.01M $CaCl_2$ was added to 2 g of soil or sediment and shaken at 25°C for 2 hours. ^{14}C levels were measured in the clear solution removed after centrifugation, and adsorption to the soil or sediment was calculated. Desorption was measured by adding 10 ml aqueous 0.01M $CaCl_2$ to the same tube with further shaking for 2 hours at 25°C. ^{14}C was measured after centrifugation and desorption was calculated. The results are shown in Table 22. Recoveries of ^{14}C ranged from 101% to 109%.

On the basis of the K_{oc} values 4'-OH-Pyr was rated as having slight to low mobility in most agricultural soils and having a slight chance of leaching.

Table 22. Properties and adsorption and desorption constants of 4'-OH-Pyr for a sediment and four agricultural soils (Fathulla *et al.*, 1995a).

Soil	Soil properties						Adsorption		Desorption	
	sand	silt	clay	organic matter	pH	CEC, meq/100 g	K_d	K_{oc}	K_d	K_{oc}
Lake sediment	93%	6.0%	1.2%	0.17%	8.2	0.85	2.76	2760	47.5	47500
Sand	92%	3.6%	4.4%	0.22%	6.0	0.82	5.50	4250	36.3	28050
Sandy loam	75%	18%	7.2%	0.96%	6.9	6.6	21.5	3810	164	29100
Silt loam	35%	54%	11%	1.8%	6.9	8.9	32.8	3060	386	36000
Clay loam	33%	28%	39%	2.1%	7.9	15.8	11.5	920	239	19100

[*Pyridyl*-^{14}C]PYPAC at 20, 100, 200 and 1000 ng/g dissolved in 10 ml aqueous 0.01M $CaCl_2$ was added to 4.9 g of soil or sediment and shaken at 25°C for 8 hours. Adsorption and desorption were determined as before (Table 23). Recoveries of ^{14}C ranged from 100% to 106%.

The results indicated that PYPAC had a high or very high mobility with a high potential to leach to ground-water on the basis of the interpretations of K_d and K_{oc} by Cohen *et al.* (1984). PYPAC is quite soluble in water, so weak sorption by soil is not surprising. Whether the potential to be leached is realised will depend on the persistence of PYPAC in soil and the prevailing field conditions.

Table 23. Adsorption and desorption constants of [*pyridyl*-^{14}C]PYPAC on the sediment and soils of Table 22 (Fathulla *et al.*, 1995b).

Soil	Adsorption		Desorption	
	K_d	K_{oc}	K_d	K_{oc}
Lake sediment	0.12	120	0.88	881
Sand	0.11	85	0.45	350
Sandy loam	0.12	21	0.84	148
Silt loam	0.34	32	1.05	98
Clay loam	0.11	9	0.72	57

Takahashi *et al.* (1988) exposed [*phenyl*-^{14}C] and [*pyridyl*-^{14}C]pyriproxyfen on upland sandy loam and silt loam soils at approximately 100 mg/m^2 to natural sunlight for 8 weeks. The soils were in layers of approximately 0.5 mm. Volatiles were collected and soil samples were taken at intervals for analysis and identification of the residues by TLC. In control samples (vials wrapped in aluminium foil) run simultaneously, 87% or more of the applied ^{14}C was still in pyriproxyfen after the 8 weeks. In the sandy loam soil pyriproxyfen disappeared with half-lives of 12.5 weeks for the phenyl label and 10.3 weeks for the pyridyl label. The mineralization half-life (production of $^{14}CO_2$) was 37 weeks for the phenyl label and 350 weeks for the pyridyl label. In the silt loam soil pyriproxyfen disappeared very quickly in the first week, but with half-lives after the first week of 18 and 21 weeks for the phenyl and pyridyl labels respectively. The corresponding mineralization half-lives were 51 and 150 weeks. The identified decomposition products of pyriproxyfen were all minor and may have arisen from other routes of degradation as well as photolysis: 4'-OH-Pyr, DPH-Pyr, POPA, POP and 2-OH-PY.

Fathulla *et al.* (1995e) irradiated phenyl- and pyridyl-labelled pyriproxyfen on a sandy loam soil at approximately 0.3 mg/kg with artificial sunlight (xenon lamp) for 20 and 18 days (12 hours irradiation per day). Volatiles were collected and soil samples taken at intervals for analysis by TLC. Control samples stored in the dark at 25°C were run simultaneously. Recoveries of ^{14}C were between 92% and 106%. The results are shown in Tables 24 and 25.

Degradation was faster in the irradiated soils than in the controls. Half-lives of [*phenyl*-^{14}C]pyriproxyfen were 16 days irradiated and 27 days dark, and of [*pyridyl*-^{14}C]pyriproxyfen 6.8 days irradiated and 13 days dark. PYPAC was identified as a degradation product reaching its maximum level on day 10. The levels of 4'-OH-Pyr after 10 days were lower in the irradiated soil than in the control, so if it was formed by photolysis it was also degraded by photolysis. The production of volatile ^{14}C was negligible. The main degradation products were, or were incorporated into, polar and unextractable compounds.

Table 24. Degradation of [*phenyl*-^{14}C]pyriproxyfen at 0.3 mg/kg on a sandy loam soil during irradiation with simulated sunlight (Fathulla *et al.*, 1995e).

Days	^{14}C, % of applied							
	pyriproxyfen		polar		4'-OH-Pyr		unextractable	
	irradiated	dark	irradiated	dark	irradiated	dark	irradiated	dark
0	100	100	nd	nd	nd	nd	0.8	0.8
2	90	95	nd	nd	nd	nd	9.1	4.2
4	90	94	2.7	nd	0.6	nd	4.4	6.3
7	65	92	10.6	1.9	2.8	2.4	14	8.4
10	44	79	22	6.3	3.5	1.9	26	12.4
14	57	81	11.5	4.4	1.3	2.0	21	10.9
20	45	57	9.1	18	1.4	2.4	35	19

Table 25. Degradation of [*pyridyl*-^{14}C]pyriproxyfen at 0.3 mg/kg on a sandy loam soil during irradiation with simulated sunlight (Fathulla *et al.*, 1995e).

Days	^{14}C, % of applied											
	pyriproxyfen		polar		PYPAC		4'-OH-Pyr		DPH-Pyr		unextractable	
	irradiated	dark	irradiated	dark	irradiated	dark	irradiated	dark	irradiated	dark	irradiated	dark
0	101	101	nd	nd	nd	nd	nd	nd	nd	nd	0.6	0.6
3	93	98	nd	nd	nd	nd	nd	nd	nd	nd	7.1	3.5
6	67	95	8.4	1.7	9.8	0.5	nd	nd	nd	nd	9.3	7.4
10	49	80	11	6.8	13	3.8	nd	nd	nd	nd	19	9.9
14	25	63	19	10	5.9	5.4	0.7	1.3	nd	nd	41	15
18	18	36	18	18	2.6	7.6	1.0	5.6	0.3	0.6	45	25

In a confined rotational crop study, Waller (1996) applied [*phenyl*-^{14}C] and [*pyridyl*-^{14}C]pyriproxyfen to a sandy loam soil at 0.20 kg ai/ha, and after an ageing interval of 30 days sowed lettuce, radish and wheat seed. Levels of ^{14}C were measured in the crops at harvest (Table 26). The levels in lettuce leaves, radish roots and leaves, and wheat forage were very low, suggesting that residue uptake was negligible. The ^{14}C residues in wheat grain, straw and chaff were investigated further. The grain was extracted with hexane/methanol, but 89% of the residue was unextractable. Mild acid hydrolysis of the extracted grain released little ^{14}C. Hydrolysis at 80°C in 6N HCl released most of the ^{14}C, but it was not organosoluble and pyriproxyfen and its immediate degradation products were not detectable, suggesting that the ^{14}C had been incorporated into proteins and carbohydrates. Extraction and hydrolysis of wheat straw and chaff gave similar results. Residues of pyriproxyfen and its immediate degradation products should not occur above negligible levels in rotational crops following the use of pyriproxyfen on the previous crop.

Table 26. Levels of ^{14}C in rotational crops sown 30 days after treatment of the soil with ^{14}C-pyriproxyfen (Waller, 1996).

Sample	Interval from sowing to harvest, days		^{14}C as pyriproxyfen, mg/kg	
	phenyl label	pyridyl label	phenyl label	pyridyl label
Lettuce leaf	43	45	0.0034	0.0065
Radish root	50	52	0.0018	0.0049
Radish leaf	50	52	0.0043	0.011
Wheat forage	36	38	0.0051	0.011
Wheat grain	123	137	0.081	0.059
Wheat straw	123	137	0.032	0.059
Wheat chaff	123	137	0.040	0.082

In a field dissipation study, pyriproxyfen as an EC formulation was applied twice at 0.15 kg ai/ha to bare ground at a field site in California intended for cotton production (Pensyl, 1995a). Soil cores (90 cm depth) were taken at intervals and sections of the cores were analysed for pyriproxyfen, 4'-OH-Pyr and PYPAC. The test area was flat with no appreciable slope. The top 30 cm of the soil was classified as a sandy loam (60% sand, 28% silt, 12% clay, 0.6% organic matter, pH 8.6) and the 30-60 cm depth as a loam. Rainfall was supplemented by irrigation and during the 7 months of the study the total rainfall plus irrigation was 30 cm.

Pyriproxyfen was detected essentially only in the top 7.5 cm of soil, apart from traces appearing in the 7.5-15 cm segment on the day of the second treatment and the following day (Table 27). The estimated half-life of pyriproxyfen in the top 7.5 cm of the soil was 16 days. Pyriproxyfen residues did not migrate down the soil profile. All the core samples analysed for pyriproxyfen were also analysed for PYPAC and 4'-OH-Pyr. PYPAC was not detected (<0.01 mg/kg) in any sample, and 4'-OH-Pyr was detected only in one sample at 0.01 mg/kg in the 7.5-15 cm layer immediately after the second application.

Table 27. Residues of pyriproxyfen in the soil profile after two applications to bare ground at 0.15 kg ai/ha in California (Pensyl, 1995a). Three soil cores were analysed on each occasion.

Day[1]	Pyriproxyfen, mg/kg, at depths of			
	0-7.5 cm	7.5-15 cm	15-30 cm	30-90 cm
-13	0.11 0.12 0.12	<0.01 (3)	<0.01 (3)	
0	0.08 0.12 0.07	<0.01 0.02 <0.01	<0.01 (3)	<0.01 (3)[2]
1	0.12 0.14 0.26	0.02 <0.01 <0.01	<0.01 (3)	
3	0.05 0.08 0.01	<0.01 (3)	<0.01 (3)	
7	0.04 0.06 0.03	<0.01 (3)	<0.01 (3)	
10	0.03 0.02 0.03	<0.01 (3)	<0.01 (3)	
14	0.05 0.04 0.09	<0.01 (3)	<0.01 (3)	
28	0.04 0.07 0.03	<0.01 (3)	<0.01 (3)	
40	0.01 (3)	<0.01 (3)	<0.01 (3)	
60	<0.01 (3)	<0.01 (3)	<0.01 (3)	
91	0.01 0.01 <0.01	<0.01 (3)	<0.01 (3)	<0.01 (3)[2]
119	<0.01 (3)	<0.01 (3)	<0.01 (3)	
184	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)[2]

[1] The first application of pyriproxyfen was on day -13 and the second on day 0
[2] Not detected (<0.01 mg/kg) in the soil layers 30-45 cm, 45-60 cm, 60-75 cm and 75-90 cm

An identical study was carried out at a field site intended for cotton production in Mississippi (Pensyl, 1995b). The treated test plot was approximately 10 m × 10 m and the area was relatively flat with 0.5-2% slope. The top 30 cm of the soil was classified as a silt loam (32% sand, 52% silt, 16% clay, 0.8% organic matter, pH 5.9) and the 30-60 cm depth as a clay loam. Rainfall was supplemented by irrigation and during the 2 months of the study the total rainfall plus irrigation was 17 cm.

Pyriproxyfen disappeared quickly from the top 7.5 cm of soil with an estimated half-life of 3.5 days. Residues were not detected further down the profile, implying that it was rapidly degraded rather than lost by mobility and dilution. PYPAC was detected at 0.01 mg/kg in only one sample, a surface soil on the day of the second application. 4'-OH-Pyr was present at 0.02 mg/kg in 2 of 3 surface core samples on day 10, at 0.02 mg/kg in 1 core sample at 30-45 cm on day 7 and at 0.01 mg/kg in 1 core, also on day 7. These sporadic occurrences of 4'-OH-Pyr at levels near the LOD are difficult to interpret as the result of systematic persistence and mobility down the soil profile.

Table 28. Residues of pyriproxyfen in the soil profile after two applications to bare ground at 0.15 kg ai/ha in Mississippi (Pensyl, 1995b). Three soil cores were analysed on each occasion.

Day[1]	Pyriproxyfen, mg/kg, at depths of			
	0-7.5 cm	7.5-15 cm	15-30 cm	30-45 cm
-14	0.06 0.06 0.06	<0.01 (3)	<0.01 (3)	
0	0.17 0.15 0.12	<0.01 (3)	<0.01 (3)	<0.01 (3)
1	0.36 0.20 0.10	<0.01 (3)	<0.01 (3)	
3	0.13 0.10 0.11	<0.01 (3)	<0.01 (3)	
7	0.02 0.06 0.05	<0.01 (3)	<0.01 (3)	
10	0.03 0.01 0.04	<0.01 (3)	<0.01 (3)	
14	<0.01 (3)	<0.01 (3)	<0.01 (3)	
28	<0.01 (3)	<0.01 (3)	<0.01 (3)	
42	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)

[1] The first application of pyriproxyfen was on day -14 and the second on day 0.

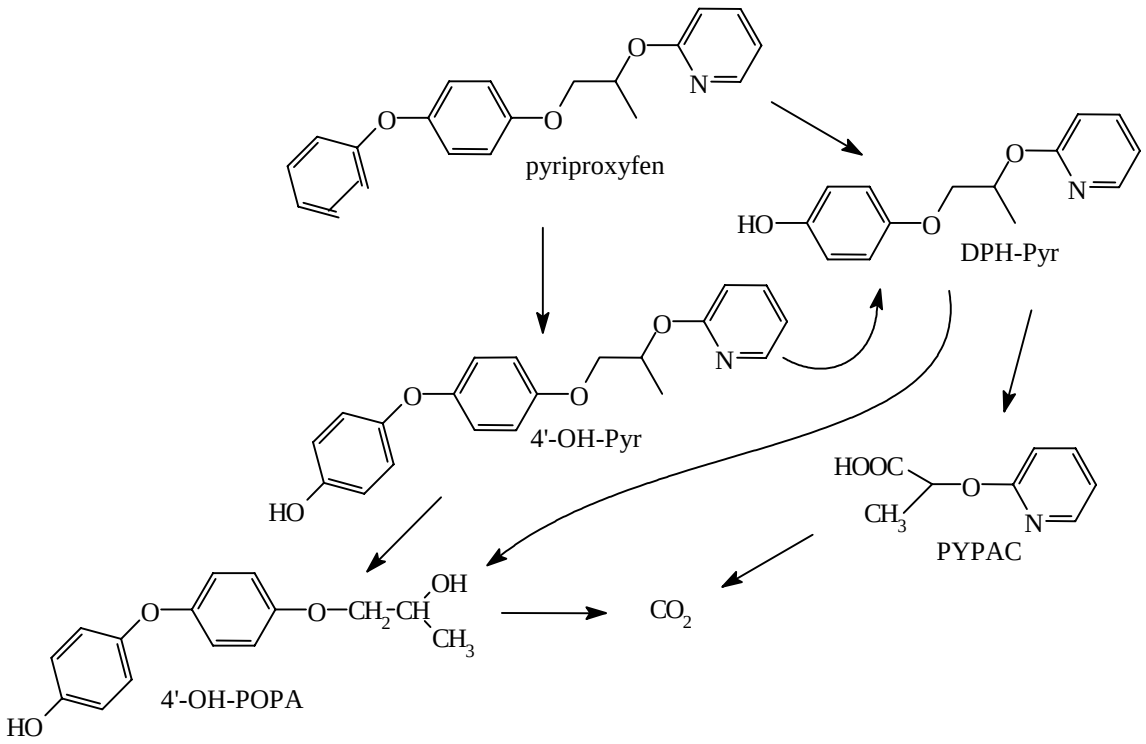


Figure 5. Fate of pyriproxyfen in soil.

Environmental fate in water/sediment systems

Fathulla *et al.* (1993b) incubated lake water (20 ml) and lake sediment (2 g) with [*phenyl*-^{14}C] and [*pyridyl*-^{14}C]pyriproxyfen at approximately 0.3 µg/g sediment in the dark at 25°C under aerobic conditions for 31 and 28 days. The sediment and water contained a large number of aerobic micro-organisms. The pH of the lake water was 8.0 with an alkalinity of 205 mg/l as $CaCO_3$. Residues were identified by HPLC and two-dimensional TLC. Recoveries of ^{14}C in the two experiments were in the range 89-105%.

The half-life of [*phenyl*-^{14}C]pyriproxyfen was 16 days. Pyriproxyfen itself was the main residue component in the sediment throughout the study (Table 29). A mixture of unidentified polar compounds accounted for 35% of the original ^{14}C by day 31. The main identified product in both water and sediment was 4'-OH-Pyr.

The half-life of [*pyridyl*-^{14}C]pyriproxyfen was 21 days. Levels of the parent compound and 4'-OH-Pyr (Table 30) were in general agreement with those from the phenyl label. From day 12 PYPAC became a substantial part of the residue in the water phase.

Table 29. Residues in a lake sediment and water resulting from aerobic incubation at 25°C with [*phenyl*-^{14}C]pyriproxyfen at approximately 0.3 µg/g sediment (Fathulla 1993b).

Days	^{14}C, % of applied.								
	Pyriproxyfen		Unidentified polar		DPH-Pyr		POP	4'-OH-Pyr	
	water	sed	water	sed	water	sed	water	water	sed
0	68	23	nd		nd		nd	nd	nd
1	52	34	nd		nd		nd	nd	nd
2	18	57	nd		nd		nd	3.8	4.5
4	19	59	nd		nd		nd	4.3	5.2
7	16	58	3.7		nd		nd	3.9	5.6
14	7.3	46	12	0.6	1.4	1.4	1.0	0.6	6.4
21	0.3	28	20	8.8	1.6	nd	0.6	2.9	10.7
31	nd	27	24	11.3	nd	nd	nd	nd	3.6

nd: not detected

Table 30. Residues in a lake sediment and water resulting from aerobic incubation at 25°C with [*pyridyl*-^{14}C]pyriproxyfen at approximately 0.3 µg/g sediment (Fathulla 1993b).

Days	^{14}C, % of applied.							
	pyriproxyfen		PYPAC		DPH-Pyr		4'-OH-Pyr	
	water	sed	water	sed	water	sed	water	sed
0	23	64	nd	nd	nd		0.2	nd
1	52	40	nd	nd	nd		0.3	nd
2	34	53	nd	4.1	nd	nd	nd	0.4
4	39	53	nd	1.7	nd	nd	1.0	0.5
7	20	65	nd	0.5	0.6	nd	4.4	3.1
12	9.3	52	11.7	0.9	nd	0.2	1.2	2.8
21	0.5	37	30	3.7	2.3	0.5	nd	4.0
28	0.3	46	25	2.8	nd	0.5	2.3	0.5

nd: not detected

An essentially identical experiment (Fathulla *et al.,* 1995c) was carried out under anaerobic conditions for 1 year. The sediment and water contained a large number of aerobic micro-organisms and some anaerobic spores. The lake water had an alkalinity of 205 mg/l expressed as $CaCO_3$. The sediment was extracted with methanol/water and acetone/water for analysis by HPLC and two-dimensional TLC as before. Recoveries of ^{14}C were in the range 90-107%. The results are shown in Tables 31 and 32.

Pyriproxyfen was the main residue in both labelled systems throughout the studies and was mainly in the sediment rather than the water. Pyriproxyfen in the phenyl-label experiment appeared to be degraded in two phases, slowly for 180 days (estimated half-life 750 days) and then more quickly for the next 6 months (estimated half-life 105 days). The likely explanation is the adaptation of the anaerobic organisms to the conditions and substrate during the 6 months. The estimated half-life of the pyridyl-labelled pyriproxyfen was 280 days. There may again have been a two-phase degradation with the second phase beginning after 9 months, but such an interpretation would rely on only the analysis at 12 months. The identified products were mainly at very low levels. PYPAC accounted for 16% of the dose after a year; because of its solubility it was mainly in the water. Volatile ^{14}C, including $^{14}CO_2$, was negligible. Much more polar material was formed from the phenyl-labelled compound, suggesting that the phenolic compounds released after the separation of PYPAC were incorporated into the humin in the sediment.

Table 31. Residues in a lake sediment and water resulting from anaerobic incubation at 25°C with [*phenyl*-^{14}C]pyriproxyfen at 0.28 µg/g sediment (Fathulla *et al.*, 1995c).

Days	^{14}C, % of applied									
	pyriproxyfen		Polar		4'-OH-Pyr		DPH-POPA		DPH-Pyr	
	water	sed	water	sed	water	sed	water	sed	water	sed
0	28	74	nd	nd	nd	nd	nd	nd	nd	nd
7	13.4	90	nd	nd	nd	nd	nd	nd	nd	nd
14	7.5	87	nd	nd	nd	nd	nd	nd	nd	nd
32	5.5	92	nd	nd	nd	nd	nd	nd	0.5	nd
61	2.1	92	0.3	nd	nd	nd	nd	nd	0.2	nd
91	2.7	89	0.1	nd	nd	nd	nd	nd	0.1	nd
120	3.1	90	0.4	0.8	nd	0.2	nd	nd	0.1	0.1
180	3.4	80	0.7	0.1	nd	0.2	nd	nd	0.1	0.1
273	5.9	52	0.9	1.1	2.2	5.2	0.5	nd	2.8	0.4
368	nd	24	13.5	0.8	nd	2.4	nd	0.2	nd	1.1

nd: not detected

Table 32. Residues of pyriproxyfen and metabolites in a lake sediment and water resulting from anaerobic incubation at 25°C of [*pyridyl*-^{14}C]pyriproxyfen at 0.28 µg/g sediment (Fathulla *et al.*, 1995c).

Days	^{14}C, % of applied											
	pyriproxyfen		polar		PYPAC		PYPA		4'-OH-Pyr		DPH-Pyr	
	water	sed	water	sed	water	sed	water	sed	water	sed	water	sed
0	20	78	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
7	13.3	83	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
14	13.3	77	nd	nd	nd	nd	nd	nd	nd	nd	nd	nd
30	5.2	89	nd	nd	nd	nd	0.2	nd	nd	nd	nd	nd
59	2.6	90	0.1	nd	<0.1	nd	0.1	nd	nd	nd	nd	nd
91	1.7	89	0.8	1.5	1.0	nd	1.3	nd	nd	nd	0.4	nd
120	2.5	82	2.4	2.2	1.2	nd	1.0	0.3	nd	nd	nd	nd
175	3.9	66	0.9	1.0	4.7	nd	1.8	0.4	nd	0.8	0.1	0.3
268	5.5	62	0.4	1.5	1.8	nd	1.0	0.7	1.4	1.4	3.6	nd
363	nd	34	1.6	1.0	16.4	0.3	nd	nd	nd	1.6	nd	0.7

nd: not detected

Itoh *et al.* (1988a) dissolved [*phenyl*-^{14}C] and [*pyridyl*-^{14}C]pyriproxyfen at nominal concentrations of 0.2 mg/l in the presence of Tween 85 at 7.5 mg/l in sterilized distilled water and sterilized Muko River water and exposed the solutions to sunlight for about 8 h/day for 5 weeks at Hyogo, Japan, approximately 40° N. Pyriproxyfen was degraded with half-lives of 17.5 and 21 days in the distilled water and river water respectively, and was essentially stable in the dark controls. A theoretical half-life of 16 days was calculated for 40° N latitude from the quantum yield for pyriproxyfen photolysis. The main photoproducts were PYPA and CO_2, accounting for 16-30% and 11-29% of the applied ^{14}C respectively. POPA, POP and DPH-Pyr were minor identified products.

Fathulla *et al.* (1995d) exposed [*phenyl*-^{14}C] and [*pyridyl*-^{14}C]pyriproxyfen dissolved at 0.1 mg/kg in sterile aqueous buffer solutions at pH 7 to continuous artificial sunlight (xenon lamp, filtered to restrict UV light below 290 nm) for 14 days at 25°C. Recoveries of ^{14}C at the various sampling times ranged from 92% to 107%. Photolysis products were identified by TLC. Negligible amounts of volatile ^{14}C, including $^{14}CO_2$, were produced.

Pyriproxyfen decreased to 24% of the phenyl and 4.7% of the pyridyl-labelled compound by day 14, with estimated half-lives of 6.4 and 3.7 days respectively. No significant degradation was observed in the dark controls. The only major identified product was PYPA, accounting for 26% of

the initial ^{14}C on day 4 and 70% on day 14. Other photolytic products were not identified but consisted of a mixture of polar materials, probably polymerised phenolic and quinonoid compounds.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods of residue analysis for pyriproxyfen and its degradation products in crops, animal products, soils and water were reported.

Gardner (1997) described analytical procedure CHE 33383-02R for pyriproxyfen in citrus peel and pulp. Samples were extracted with acetone, the extract was diluted with sodium chloride solution and partitioned with dichloromethane. This solution was cleaned up by column chromatography, on silica gel for peel and on Florisil for pulp. The eluates were evaporated and the residues taken up in toluene for analysis by GLC with an NPD. The LOD was 0.01 mg/kg.

Benwell (1997a) validated the method. Analytical recoveries from peel and pulp fortified at 0.01, 0.10 and 1.00 mg/kg were mean 95%, range 90-102% (n = 9) for peel and mean 84%, range 73-96% (n = 9) for pulp.

Van Zyl (1997) used the analytical method described by Kakuta *et al.* (1989) for pyriproxyfen in citrus whole fruit, peel and pulp in the South African citrus trials. The method was essentially that described by Gardner (1997). Analytical recoveries from samples fortified at 0.01-1.00 mg/kg were whole fruit mean 94%, range 70-108% (n = 5), peel mean 91%, range 82-108% (n = 13) and pulp mean 102%, range 87-110% (n = 13). The LOD was 0.01 mg/kg.

Orpella *et al*. (1997) used a method similar to CHE 33383-02R with the Florisil clean-up for the determination of pyriproxyfen residues in tomatoes. Analytical recoveries from tomatoes fortified at 0.01, 0.10 and 1.00 mg/kg were mean 102%, range 92-109% (n = 15). The LOD was 0.01 mg/kg.

Kruplak (1996a) described method RM-33P-2-2 (a modification of RM-33/P-2; see below) for pyriproxyfen and PYPAC residues in cotton seed. The residues were extracted in a blender with acetonitrile/water (4:1) and the filtrate was mixed with ethyl acetate to prevent foaming during rotary evaporation to an aqueous phase. This was diluted with 5% aqueous sodium chloride and the pyriproxyfen was extracted into dichloromethane; PYPAC remained in the water. The dichloromethane was evaporated to leave a residue which was taken up in hexane and acetonitrile. The acetonitrile layer was evaporated and the residue taken up in hexane and cleaned up on a silica gel column. Pyriproxyfen was determined by GLC with an NP detector. The aqueous phase containing PYPAC was acidified and the PYPAC extracted into ethyl acetate. The solvent was evaporated just to dryness and the PYPAC methylated by treatment with methyl iodide in methanolic tetrabutylammonium hydroxide at 45-50°C for 2 hours. After careful evaporation of the solvent the residue was taken up in hexane/ethyl acetate and cleaned up on a disposable silica gel column for GLC with an NP detector. The validated LOD for both compounds was 0.02 mg/kg. A trained analyst could analyse a set of 8 samples for pyriproxyfen and PYPAC in approximately 16 hours. Analytical recoveries from cotton seed fortified at 0.02 and 0.1 mg/kg were pyriproxyfen mean 87%, range 81-89% (n = 4); PYPAC mean 83%, range 72-95% (n = 4).

Pensyl (1996a) validated method RM-33P-2 for pyriproxyfen and PYPAC in cotton seed. RM-33P-2 was modified successively to RM-33P-2-3 after experience and suggestions from an independent laboratory. The LOD for both analytes was 0.02 mg/kg. Analytical recoveries from cotton seed fortified at 0.02 and 0.1 mg/kg were pyriproxyfen mean 76%, range 67-90% (n = 9); PYPAC mean 81%, range 79-90% (n = 9). Pensyl (1996b) used method RM-33P to determine

pyriproxyfen, PYPAC and DPH-Pyr in samples from the US supervised trials on cotton in 1994 and 1995. The results, corrected for control values, are shown in Table 33.

Table 33. Procedural recoveries of pyriproxyfen and metabolites from samples from the US supervised cotton trials in 1994 and 1995 (Pensyl, 1996b).

Compound	Sample	Fortification, mg/kg	Mean recovery, %	Range, %	No. of analyses
Pyriproxyfen	cotton seed	0.02	88	74-102	14
Pyriproxyfen	cotton seed	0.10	88	68-136	20
PYPAC	cotton seed	0.02	77	62-105	15
PYPAC	cotton seed	0.10	79	66-99	21
Pyriproxyfen	gin trash	0.02	100	47-119	5
Pyriproxyfen	gin trash	0.10	91	81-99	10
DPH-Pyr	gin trash	0.02	96	77-124	7
DPH-Pyr	gin trash	0.10	102	86-146	11
Pyriproxyfen	meal	0.02, 0.10		75-76	2
Pyriproxyfen	hulls	0.02, 0.10		70-75	2
Pyriproxyfen	crude oil	0.02, 0.10	89	75-101	6
Pyriproxyfen	refined oil	0.02, 0.10		97	2
PYPAC	meal	0.02, 0.10		64-78	2
PYPAC	hulls	0.02, 0.10		69-73	2
PYPAC	crude oil	0.02, 0.10	75	72-80	6
PYPAC	refined oil	0.02, 0.10		51-64	2

Green (1997) analysed milk for pyriproxyfen, POP and 4'-OH-Pyr by method RM-33G-2 and for 2,5-OH-Py by RM-33G-3. The methods include an acid hydrolysis step to release POP and 4'-OH-Pyr from conjugates. In G-2 milk was extracted with an ethyl acetate/methanol mixture, and the solvent evaporated to leave an aqueous solution which was extracted with ethyl acetate. The residue in the ethyl acetate was further cleaned up by acetonitrile/hexane partitioning and an aliquot was purified on an alumina column and analysed for pyriproxyfen by GLC with an NPD. A second portion of the aqueous residue after evaporation of the original ethyl acetate/methanol extract was hydrolysed with 1N HCl for 2 hours to convert the conjugates to free POP and 4'-OH-Pyr, which were cleaned up on a silica gel column and determined by HPLC with a UV detector (275 nm). Analytical recoveries from 22 samples of milk fortified at 0.02 or 0.10 mg/kg were pyriproxyfen mean 90%, range 71-104%, POP mean 93%, range 76-115% and 4'-OH-Pyr mean 84%, range 69-105%.

RM-33G-3 for 2,5-OH-Py and its conjugates was similar to RM-33G-2, except that the extract was cleaned up on a benzenesulfonic acid column after hydrolysis. Free 2,5-OH-Py was then determined by HPLC with fluorescence detection (excitation 320 nm, emission 395 nm). Recoveries from milk fortified at 0.02 and 0.10 mg/kg were mean 96%, range 66-129% (n = 24).

Green (1997) also analysed muscle, fat, liver and kidneys for pyriproxyfen by method RM-33T-1 and for 4'-OH-Pyr by RM-33T-2, and liver and kidneys for POP by RM-33T-3 and for 2,5-OH-Py by RM-33T-4. These methods are essentially identical to RM-33-G2 and -G3 except that the HPLC of POP was with fluorescence detection (excitation 235, emission 327 nm). Analytical recoveries at 0.02 and 0.10 mg/kg were pyriproxyfen mean 93%, range 87-99% (n = 8); 4'-OH-Pyr mean 81%, range 68-88% (n = 8); POP mean 83%, range 69-106% (n = 8); 2,5-OH-Py mean 86%, range 73-96% (n = 6). The LODs were typically 0.01-0.02 mg/kg.

Pensyl (1994a,b) described method RM-33S-1 for pyriproxyfen and PYPAC, and RM-33S-2 for 4'-OH-Pyr in soil. In 33S-1 residues were extracted with methanol/0.1N NaOH and the methanol evaporated. The remaining aqueous solution was diluted with sodium chloride solution and the pyriproxyfen extracted with dichloromethane; PYPAC remained in the aqueous phase. The dichloromethane was evaporated and the residues were taken up in hexane/ethyl acetate and cleaned

up on an alumina column for GLC with an NPD. The aqueous solution containing PYPAC was acidified with hydrochloric acid and extracted with ethyl acetate. The extract was evaporated, the residue methylated with methyl iodide in methanolic tetrabutylammonium hydroxide and, after evaporations and extractions, taken up in hexane/ethyl acetate for GLC with an NPD. Care must be taken during evaporation of methyl PYPAC or residues will be lost. The LOD for both analytes was 0.01 mg/kg. Analytical recoveries from soil fortified at 0.02 and 0.1 mg/kg were pyriproxyfen mean 91%, range 88-95% (n = 9); PYPAC mean 74%, range 69-79% (n = 12); 4-OH-Pyr mean 94%, range 74-105% (n = 12). RM-33S-2 was superseded by RM-33S-3-3, described below.

Pensyl (1995a,b) used methods RM-33S-1 and RM-33S-2 for soil analyses in field dissipation studies. The procedural recoveries are shown in Table 34.

Table 34. Procedural recoveries of pyriproxyfen and degradation products from soil in field dissipation studies (Pensyl, 1995a,b).

Compound	Location	Fortification, mg/kg	Mean recovery, %	Range, %	No. of analyses
Pyriproxyfen	CA	0.02	97	73-146	19
Pyriproxyfen	MS	0.02	86	66-106	15
Pyriproxyfen	CA	0.10	106	74-129	20
Pyriproxyfen	MS	0.10	101	78-119	15
PYPAC	CA	0.02	67	52-87	16
PYPAC	MS	0.02	72	59-90	14
PYPAC	CA	0.10	73	49-97	15
PYPAC	MS	0.10	83	66-100	14
4'-OH-Pyr	CA	0.02	107	80-168	16
4'-OH-Pyr	MS	0.02	80	62-134	18
4'-OH-Pyr	CA	0.10	113	98-131	17
4'-OH-Pyr	MS	0.10	105	81-123	18

Kruplak (1996b) validated method RM-33S-1-5 for pyriproxyfen and PYPAC in soil. The residues were extracted with methanol/0.1N NaOH, the methanol was evaporated and the extract diluted with water, adjusted to pH 7 and extracted with dichloromethane. Pyriproxyfen was in the dichloromethane phase and PYPAC in the aqueous phase. The remainder of the procedure followed that of RM-33P-2-2 for cotton seed. The author stressed the care necessary during the evaporation of solutions of methylated PYPAC, which may easily be lost because of its volatility. Analytical recoveries from soil fortified at 0.02 and 0.1 mg/kg were pyriproxyfen mean 91%, range 88-92% (n = 4); PYPAC mean 97%, range 85-115% (n = 4).

Kruplak (1996c) described method RM-33S-3-3, a development of RM-33S-2, for the determination of 4'-OH-Pyr. Soil was extracted with a methanol/phosphate buffer and the filtrate evaporated to yield an aqueous concentrate which was mixed with sodium chloride solution and extracted with ethyl acetate. The ethyl acetate was evaporated to leave a residue that was taken up in hexane/ethyl acetate for clean-up on a disposable silica gel column. The eluate was evaporated to dryness and the residue taken up in methanol/water for reversed-phase HPLC analysis with fluorescence or UV detection. The LOD was 0.02 mg/kg. A trained analyst can complete the analysis of a set of 8 samples in about 8 hours. Analytical recoveries from soil fortified at 0.02 and 0.1 mg/kg were mean 92%, range 78-99% (n = 4).

Nandihalli (1996) determined the recoveries of pyriproxyfen and PYPAC by an FDA multi-residue GLC method from fortified cotton seed and apple samples, representing fatty and non-fatty foods. Adequate recoveries of pyriproxyfen were achieved at 0.05 and 0.5 mg/kg, but PYPAC was not recovered from the Florisil column clean-up.

Schuster (1989) validated the analytical method for pyriproxyfen in aquarium water used in the ecotoxicology tests. The residues were extracted with dichloromethane, the dichloromethane was

evaporated and the residue was taken up in hexane for analysis by GLC with an NPD. The validated LOD was 1 µg/l. Recoveries over the concentration range 1.15 µg/l to 11.5 mg/l were mean 105%, range 102-111% (n = 10).

Stability of pesticide residues in stored analytical samples

Green (1997) stored cattle tissue samples fortified with pyriproxyfen and metabolites at -20ºC (Table 35). When pyriproxyfen was stored with liver, fat and muscle for 1 month the estimated times for 30% decrease were 45, 55 and 68 days respectively. 4'-OH-Pyr was stored 96 days in fat and 71 days in muscle where the estimated times for 30% decrease were 200 and 90 days respectively. 4'-OH-Pyr sulfate and POP sulfate were stored with liver for about 2 months; the estimated times for 30% decrease of the conjugate + free metabolite were 110 days and 66 days respectively. 2,5-OH-Py in kidneys decreased by 30% in an estimated 24 days.

Table 35. Freezer storage stability of pyriproxyfen and metabolites in muscle, fat, liver and kidneys fortified at 0.1 mg/kg and stored at –20ºC (Green, 1997). The % remaining is not corrected for the corresponding procedural recovery.

Compound	Sample	Storage period, days	Procedural recovery, %	% remaining	Estimated time for 30% decrease, days
Pyriproxyfen	liver	0	86	100, 103	
Pyriproxyfen	liver	15	104	90 86	
Pyriproxyfen	liver	32	105	79 79	45 days
Pyriproxyfen	muscle	0		91 95	
Pyriproxyfen	muscle	16	88	71 80	
Pyriproxyfen	muscle	31	102	82 76	68 days
Pyriproxyfen	fat	0		90 93	
Pyriproxyfen	fat	14	96	86 86	
Pyriproxyfen	fat	33	103	78 70	55 days
4'-OH-Pyr	fat	0		76 78	
4'-OH-Pyr	fat	13	70	66 67	
4'-OH-Pyr	fat	96	74	56 67	200 days
4'-OH-Pyr	muscle	0	82	75 84	
4'-OH-Pyr	muscle	14	84	80 79	
4'-OH-Pyr	muscle	30	75	72 72	
4'-OH-Pyr	muscle	71	70	64 58	90 days
4'-OH-Pyr conj [1]	liver	0		81 84	
4'-OH-Pyr conj [1]	liver	15	70	76 77	
4'-OH-Pyr conj [1]	liver	28	77	77 76	
4'-OH-Pyr conj [1]	liver	57	66	69 67	110 days
POP conj [2]	liver	0		76 74	
POP conj [2]	liver	29	80	74 81	
POP conj [2]	liver	51	67	63 69	
POP conj [2]	liver	72	68	43 59	66 days
2,5-OH-Py	kidneys	0		86 86	
2,5-OH-Py	kidneys	22	83	71 65	
2,5-OH-Py	kidneys	53	88	48 60	
2,5-OH-Py	kidneys	119	70	16 14	24 days

[1] Fortified with the sulfate conjugate at 0.10 mg/kg expressed as 4'-OH-Pyr
[2] Fortified with the sulfate conjugate at 0.10 mg/kg expressed as POP

Goller (1998) stored tomato homogenate spiked with pyriproxyfen at 0.10 mg/kg at -18°C for 12 months. Samples were analysed by method NNA-90-0016, similar to CHE 333/83-02R. The initial acetone extract was evaporated to an aqueous solution, which was mixed with 5% sodium chloride and extracted with dichloromethane. The dichloromethane extract was evaporated and the residue taken up in hexane, cleaned up on a Florisil column and analysed by GLC with a thermionic detector. The LOD was 0.01 mg/kg.

Pyriproxyfen was stable for at least the 12 months of the study (Table 36).

Table 36. Stability of pyriproxyfen in tomato homogenate fortified at 0.10 mg/kg and stored at –18ºC (Goller, 1998). The % remaining is not corrected for the corresponding procedural recovery.

Storage period, months	Procedural recovery, %	% remaining
0	93	105, 102
1	92	89, 97
3	104	96, 101
6	84	73, 75
12	86	96, 98

Pensyl (1996b) determined the stability of pyriproxyfen, PYPAC and DPH-Pyr added to cotton seed, gin trash and oil at 0.1 mg/kg and stored at -20°C (Table 37) in conjunction with supervised residue trials on cotton. The compounds were stable for the periods tested, except that DPH-Pyr was of marginal stability in gin trash for 6 months, decreasing by 30% in about 150 days.

Table 37. Stability of pyriproxyfen and metabolites in cotton seed, gin trash and crude oil fortified at 0.1 mg/kg and stored at –20ºC (Pensyl, 1996b). The % remaining is not corrected for the corresponding procedural recovery.

Compound	Sample	Storage period, days	Procedural recovery, %	% remaining (2 stored samples)
Pyriproxyfen	cotton seed	0	89	77 83
Pyriproxyfen	cotton seed	29	136	101, 126
Pyriproxyfen	cotton seed	91	87	98, 86
Pyriproxyfen	cotton seed	395	86	75, 71
PYPAC	cotton seed	0	95	97, 99
PYPAC	cotton seed	31	83	83, 90
PYPAC	cotton seed	141	71	70, 78
PYPAC	cotton seed	380	84	83, 84
Pyriproxyfen	gin trash	0	99	89, 88
Pyriproxyfen	gin trash	71	99	106, 93
Pyriproxyfen	gin trash	231	99	72, 75
DPH-Pyr	gin trash	0	86	90, 92
DPH-Pyr	gin trash	89	102	64, 60
DPH-Pyr	gin trash	178	81	62, 55
Pyriproxyfen	cotton seed oil, crude	0	95	89, 87
Pyriproxyfen	cotton seed oil, crude	32	101	99, 99
PYPAC	cotton seed oil, crude	0	74	72, 80
PYPAC	cotton seed oil, crude	32	74	84, 82

Pensyl (1995a,b) determined the stability of pyriproxyfen, PYPAC and 4'-OH-Pyr added to California and Mississippi soil and stored at a nominal -20°C (Table 38) in conjunction with dissipation studies. The California soil was classified as a sandy loam (60% sand, 28% silt, 12% clay, 0.6% organic matter, pH 8.6) and the Mississippi soil as a silt loam (32% sand, 52% silt, 16% clay, 0.8% organic matter, pH 5.9).

Pyriproxyfen and PYPAC were stable for the periods tested (210-218 days). 4'-OH-Pyr was stable in the California soil for the 168 days of the trial, but unstable in the Mississippi soil with about half of the original concentration remaining after 3 and 7 days. All the samples of Mississippi soil analysed for 4'-OH-Pyr in the dissipation trial were therefore extracted within 3-5 days of sampling.

Table 38. Stability of pyriproxyfen and metabolites in soil samples fortified at 0.1 mg/kg and stored at –20ºC (Pensyl, 1995a,b). The % remaining is not corrected for the corresponding procedural recovery.

Compound	Location	Storage period, days	Procedural recovery, %	%, remaining, (2, stored, samples)
Pyriproxyfen	CA	0	87	74, 86
Pyriproxyfen	CA	29	86	88, 88
Pyriproxyfen	CA	116	87	94, 84
Pyriproxyfen	CA	211	106	89, 102
PYPAC	CA	0	88	72, 86
PYPAC	CA	56	98	83, 88
PYPAC	CA	150	65	73, 74
PYPAC	CA	218	84	82, 79
4'-OH-Pyr	CA	0	97	98, 106
4'-OH-Pyr	CA	1	93	91, 89
4'-OH-Pyr	CA	7	116	117, 125
4'-OH-Pyr	CA	15	125	108, 105
4'-OH-Pyr	CA	29	105	103, 110
4'-OH-Pyr	CA	99	100	111, 114
4'-OH-Pyr	CA	168	139	81, 99
Pyriproxyfen	MS	0	118	118, 120
Pyriproxyfen	MS	29	94	88, 85
Pyriproxyfen	MS	116	96	63, 69
Pyriproxyfen	MS	210	110	75, 64
PYPAC	MS	0	80	84, 79
PYPAC	MS	56	87	90, 82
PYPAC	MS	149	71	69, 63
PYPAC	MS	218	79	86, 88
4'-OH-Pyr	MS	0	87	96, 98
4'-OH-Pyr	MS	1	80	60, 62
4'-OH-Pyr	MS	3	93	52, 50
4'-OH-Pyr	MS	7	107	46, 43
4'-OH-Pyr	MS	20	118	35, 44
4'-OH-Pyr	MS	36	107	29, 26

Definition of the residue

The main residue in the metabolism studies on plant commodities was pyriproxyfen itself. In cotton seed the levels of free + conjugated PYPAC and PYPA exceeded that of pyriproxyfen, which was very low, probably because the metabolites were translocated more readily. PYPAC in cotton seed in the metabolism study was about 60% free and 40% conjugated, but in the trials on cotton free PYPAC was generally undetected and lower than pyriproxyfen in the seed.

The residue can be defined as pyriproxyfen for enforcement in crops.

In animal commodities the composition of the residue varies in different tissues. Pyriproxyfen itself is fat-soluble (log P_{OW} 5.37) so it predominates in fat. In muscle all the residues are very low, but pyriproxyfen is again the main component. In milk and liver 4'-OH-Pyr with its sulfate conjugate are the main residues, while in kidneys POP is the main residue with 4'-OH-Pyr also a significant component. Pyriproxyfen predominates in eggs.

The feeding study on dairy cows suggests that the residues in milk and tissues will generally be undetectable or very low whatever the residue definition, except pyriproxyfen itself in fat and the fat of milk at the higher dietary burdens. The Meeting agreed it would be unpractical to define the residue to include metabolites and their conjugates in liver and kidneys for undetectable residues; it would create a pointless additional analytical expense.

Pyriproxyfen is also a suitable definition of the residue for dietary intake estimates.

Proposed definition of the residue (for compliance with MRLs and for the estimation of dietary intake): pyriproxyfen.

The residue is fat-soluble.

USE PATTERN

Pyriproxyfen is an insect growth regulator with insecticidal activity against public health insect pests: houseflies, mosquitoes and cockroaches. In agriculture and horticulture pyriproxyfen has registered uses for the control of scale, whitefly, bollworm, jassids, aphids and cutworms. Registered uses of pyriproxyfen are shown in Table 39.

Table 39. Registered uses of pyriproxyfen.

Crop	Country	Form	Application					PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Water vol l/ha	No.	
Apple	Israel	EC	foliar		0.015	1500-2000	1	[1]GS
Bean	Brazil	EC	foliar	0.1		200-250	2	14
Cabbage	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Cabbage	Israel	EC	foliar	0.075		80-100		14
Carrot	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Citrus	Brazil	EC	foliar		0.005-0.0075	10 l/tree	2	14
Citrus	Cyprus	EC	foliar		0.005-0.0075		2	30
Citrus	Israel	EC	foliar	0.25-0.40	0.01	2500-4000		[2]GS
Citrus	Lebanon	EC	foliar		0.0075			30
Citrus	South Africa	EC	foliar		0.0030		3	[3]90
Citrus	Spain	EC	foliar		0.0025-0.0075		2	30
Citrus	Turkey	EC	foliar		0.005			30
Citrus	UAE	EC	foliar		0.0025-0.0075		1	[4]GS
Citrus	Zimbabwe	EC	foliar		0.0075		1	[5]90
Citrus	Zimbabwe	EC	foliar		0.0030		2	[6]90
Cotton	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Cotton	El Salvador	EC	(a) foliar	0.05		15-27	2	30
Cotton	El Salvador	EC	foliar	0.05		290	2	30
Cotton	Israel	EC	(a) foliar	0.075		30-200		30
Cotton	Israel	EC	foliar	0.075		30-200		30
Cotton	Pakistan	[8]EC	foliar	0.038-0.05				
Cotton	Sudan	[7]EC	(a) foliar	0.044		23	2	
Cotton	Turkey	EC	foliar		0.005			30
Cotton	Turkey	[8]EC	foliar	0.05				15
Cotton	USA	EC	(a) foliar	0.059-0.075		28-94	1	28
Cotton	USA	EC	foliar	0.059-0.075		94-470	1	28

[1] Until fruit set or after picking

[2] End of May in varieties picked until end of December. End of June in varieties picked after the end of December.

[3] First spray late November or December, second spray at bud burst, third spray at 80-100% petal drop or shortly thereafter.

[4] Apply at bud burst or petal drop.

[5] Apply at bud burst or at 80-100% petal drop or shortly thereafter.

[6] First spray at bud burst. Second spray at 80-100% petal drop or shortly thereafter.

[7] Formulation contains pyriproxyfen + fenpropathrin

[8] Formulation of fenpropathrin (150 g/l) and pyriproxyfen (50 g/l)

Crop	Country	Form	Application					PHI, days
			Method	Rate, kg ai/ha	Spray conc. kg ai/hl	Water vol l/ha	No.	
Cucumber	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Egg plant	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Egg plant	Israel	EC	foliar	0.075		80-100		14
Egg plant	Lebanon	EC	foliar		0.0075			30
Egg plant	Netherlands	EC	foliar	0.013-0.038	0.0025	500-1500	2 g	3
Grape-vine	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Melon	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Melon	Israel	EC	foliar	0.075		80-100		14
Okra	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Olive	Israel	EC	foliar		0.010-0.015	2000-2500		[1]GS
Peach	Israel	EC	foliar		0.015	1500-2000	1	[1]GS
Pear	Israel	EC	foliar		0.015	1500-2000	1	[1]GS
Pear	Lebanon	EC	foliar		0.0075			45
Peppers	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Peppers, sweet	Netherlands	EC	foliar	0.013-0.038	0.0025	500-1500	2 g	3
Persimmon	Israel	EC	foliar		0.007	1500		[9]GS
Plum	Israel	EC	foliar		0.015	1500-2000	1	[1]GS
Pumpkin	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Soybean	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14
Tomato	Brazil	EC	foliar		0.005-0.01	800-1000	2	7
Tomato	Lebanon	EC	foliar		0.0075			30
Tomato	Netherlands	EC	foliar	0.013-0.038	0.0025	500-1500	2 g	3
Tomatoes	Turkey	EC	foliar		0.0038		1	15
Watermelon	Brazil	EC	foliar	0.05-0.1	0.005-0.01		2	14

(a) aerial application
g: glasshouse use
GS growth stage

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting received information on supervised field trials on citrus and cotton.

Table 40 Citrus fruits (mandarin, orange, grapefruit). *Israel, Italy, South Africa, Spain.*
Table 41 Cotton seed. *USA.*
Table 42 Cotton gin trash. *USA.*

Where residues were not detected they are recorded in the Tables as below the limit of determination (LOD), e.g. <0.01 mg/kg. Residues, application rates and spray concentrations have generally been rounded to 2 significant figures or, for residues near the LOD, to 1 significant figure. Although trials included control plots, control residues are recorded in the Tables only if they exceeded the LOD. Residues are recorded uncorrected for recovery.

Oranges and mandarins were treated with pyriproxyfen in trials in Spain in 1991 by a knapsack motorised hand-lance sprayer. The plots were single trees and field samples of 1 kg or 5 fruits were harvested for analysis. Fruit were stored in a freezer for approximately 4 months before analysis. Orange trials in Spain in 1992 were similar except that the trees were sprayed to run-off and field samples of 2 kg were stored for 7-8 weeks before extraction and analysis. The field reports for the trials in study NNR-31-0021 were very brief.

[9] Until middle of June

Single mandarin trees were sprayed with a motor pump in supervised trials in Spain in 1992. Field samples of 2 kg were stored for 24 weeks before analysis. Procedural recoveries were in the range 47-78%.

In Italian trials on mandarins and oranges in 1991, pyriproxyfen was applied by knapsack motor sprayer to plots of 6 trees. Field samples of 12 fruits or 2 kg were stored for 101-117 days before analysis.

Pyriproxyfen was applied to orange and mandarin trees with a diaphragm pump and spray gun in Spain in supervised trials in 1997. Plot sizes were 8-20 trees and field samples of 2 kg or 12 fruit were analysed after very short periods in storage.

Mandarin and orange trees were treated by hand gun sprayer in South African trials in 1997. Plots were of 6 trees, and field samples of 2 kg (12-24 fruit) were stored for 14 weeks before analysis. In orange trials in 1998, plots of 4 rows of 8-10 trees were sprayed with a high-pressure pump and spray gun. Field samples of at least 2 kg (12-24 fruit) were stored for 15 weeks before analysis.

In a series of grapefruit trials in Israel in 1997 pyriproxyfen was applied by high-pressure spray gun to plots of 5 rows of 10 trees. Field samples of 13 fruits or 2 kg were stored for 233-375 days before analysis. Residues in the mature fruit were calculated from separate analyses of peel and pulp. Peel constituted 37-45% of the weight of the fruit. The trees were treated from 4 June to 10 June in the 5 trials and grapefruit were harvested from 7 October to 19 October. This is not strictly in accord with the label instructions which permit application until the end of May for varieties picked until the end of December and application until the end of June for varieties picked after the end of December. The time for a 30% residue decrease was estimated from three decline trials as 27, 51 and 75 days, demonstrating quite a slow decrease and hence sufficient latitude to interpret the timing as matching GAP conditions.

Fifteen trials on cotton in 1994 and 1995 were geographically distributed to represent 97% of the commercial cotton production area in the USA. Tractor-mounted boom sprays were used in all trials except the Californian trials in 1994 and trial V-11117-E in 1995 where backpack sprayers with hand-held booms were used. The plot sizes ranged from 4 rows of 30 m to 12 rows of 70 m. The field samples were at least 1.2 kg of undelinted seed. The longest periods of frozen storage of the samples were 157 days for pyriproxyfen determination and 180 days for PYPAC determination.

In six trials in 1995, unginned cotton (20 kg) was harvested and processed to produce gin trash (plant residues from ginning cotton - burrs, leaves, stems, lint, immature seeds), which is used as an animal feed (Table 42). Residues were determined in the samples as received, but moisture levels were measured and are recorded in Table 42.

Table 40. Pyriproxyfen residues in citrus fruit resulting from supervised trials in Israel, Italy, South Africa and Spain from 1991 to 1998. Double-underlined residues were from treatments according to GAP and are valid for the estimation of maximum residue levels.

Location, year (variety)	Application					PHI, days	Pyriproxifen, mg/kg[1]	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	kg ai/ha			
MANDARIN								
Italy (Marina), 1996 (Clementina)	EC	0.075	0.0075	1000	1	44 60	peel 0.23 pulp <0.01 wf 0.08 [2] peel 0.11 pulp <0.01 wf 0.04 [2]	NNR-0047 Pyriproxyfen-IT-1996-3
South Africa (Cape Province), 1997 (Clementine Nules)	EC	0.36	0.003	12000	1 2	63 0 30 60 90 120	0.03 0.03 0.23 0.28 0.09 0.11 0.04 0.06 peel 0.065 pulp <0.01 wf <u>0.02</u> peel 0.045 pulp <0.01 wf 0.01	NNR-0048 IK30196/97
Spain (Valencia), 1991 (Fortuna)	EC	0.08	0.005	1600	1	31 45 61	<u>0.069</u> 0.057 0.062	NNR-21-0018 S/SP/E/91971
Spain (Betera), 1992 (Fortuna)	EC		0.005		1	17 31 45 60	0.14 <u>0.20</u> 0.19 0.15	NNR-31-0022[3] S/SP/M/92163
Spain (Rafeguaraf), 1992 (Fortuna)	EC		0.005		1	16 31 45 60	0.20 <u>0.33</u> 0.30 0.28	NNR-31-0022[3] S/SP/M/92160
Spain (Murcia), 1997 (Clemenules)	EC	0.23	0.0075	3000	1 GS 77	0 60	0.48 0.03	NNR-0054S R10.A.97.026
Spain (Murcia), 1997 (Marisol)	EC	0.23	0.0075	3000	1 GS 78	0 15 30 45 60	0.23 0.18 0.09 <u>0.10</u> 0.06	NNR-0054S R10.A.97.027
ORANGE								
Italy (Marina), 1996 (Navalin)	EC	0.075	0.0075	1000	1	0 14 28 44 60	peel 0.31 pulp <0.01 wf 0.11 [2] peel 0.14 pulp <0.01 wf 0.04 [2] peel 0.12 pulp <0.01 wf 0.04 [2] peel 0.10 pulp <0.01 wf 0.03 [2] peel 0.15 pulp <0.01 wf <u>0.06</u> [2]	NNR-0047 Pyriproxyfen-IT-1996-1
Italy (Marina), 1996 (Navalin)	EC	0.075	0.0075	1000	1	44 60	peel 0.11 pulp <0.01 wf 0.04 [2] peel 0.08 pulp <0.01 wf 0.02 [2]	NNR-0047 Pyriproxyfen-IT-1996-2

Location, year (variety)	Application					PHI, days	Pyriproxifen, mg/kg[1]	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	kg ai/ha			
South Africa (Cape province), 1997 (Navel)	EC	0.36	0.003	12000	1 2	64 0 30 60 90 120	<0.01 (2) 0.10 0.11 0.03 0.03 0.02 0.02 peel 0.045 pulp <0.01 wf 0.01 peel 0.085 pulp <0.01 wf 0.02	NNR-0048 IK30296/97
South Africa (Hazyview Mpumalanga), 1998 (Valencia)	EC	0.36	0.003	12000	1 2	105 0 30 60 90 120	<0.01 0.09 0.06 peel 0.12 pulp <0.01 wf 0.04 [2] peel 0.16 pulp <0.01 wf 0.05 [2] peel 0.18 pulp <0.01 wf 0.05 [2]	NNR-0060 311P130
South Africa (Karino Irial Mpumalanga), 1998 (Valencia)	EC	0.36	0.003	12000	1 2	105 0 30 60 90 120	<0.01 0.09 0.05 peel 0.12 pulp <0.01 wf 0.04 [2] peel 0.19 pulp <0.01 wf 0.05 [2] peel 0.20 pulp <0.01 wf 0.06 [2]	NNR-0060 311P130
Spain (Valencia), 1991 (Navelate)	EC	0.08	0.005	1600	1	31 45 61	0.12 0.11 0.08	NNR-21-0018 S/SP/E/91972
Spain (Albalat), 1992 (Navel)	EC		0.005	runoff	1	17 31 45 61	0.25 0.25 0.20 0.18	NNR-31-0021 S/SP/M/92161
Spain (Betera), 1992 (Navelate)	EC		0.005	runoff	1	17 31 45 60	0.25 0.22 0.25 0.20	NNR-31-0021 S/SP/M/92162
Spain (Murcia), 1997 (Navelina)	EC	0.23	0.0075	3000	1 GS 77	0 15 30 45 60	0.17 0.10 0.06 0.08 0.04	NNR-0054S R10.A.97.025
Spain (Murcia), 1997 (New Hall)	EC	0.23	0.0075	3000	1 GS 78	0 60	0.25 0.03	NNR-00548S R10.A.97.024
GRAPEFRUIT								
Israel (Mazkeret Batyia), 1997 (Sweetie)	EC	0.35	0.01	3500	1 4 June	137 19 Oct	peel 0.07 pulp <0.01 wf 0.03 [2]	NNR-0059 1628/1
Israel (Gimzo), 1997 (Sweetie)	EC	0.4	0.01	4000	1 4 June	63 98 125 130 12 Oct	0.06 0.07 0.04 peel 0.08 pulp <0.01 wf 0.04 [2]	NNR-0059 1628/1

Location, year (variety)	Application					PHI, days	Pyriproxifen, mg/kg[1]	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	kg ai/ha			
Israel (Mesilot), 1997 (Sweetie)	EC	0.3	0.01	3000	1 8 June	0 59 94 121 7 Oct	0.37 0.13 0.09 peel 0.21 pulp <0.01 wf 0.08 [2]	NNR-0059 1628/1
Israel (Hadasim), 1997 (Sweetie)	EC	0.4	0.01	4000	1 8 June	59 94 121 126 12 Oct	0.04 0.04 0.03 peel 0.07 pulp <0.01 wf 0.03 [2]	NNR-0059 1628/1
Israel (Hadera), 1997 (Sweetie)	EC	0.35	0.01	3500	1 10 June	124 12 Oct	peel 0.06 pulp <0.01 wf 0.03 [2]	NNR-0059 1628/1

[1] wf: whole fruit
[2] Residues in whole fruit calculated from residues in peel and pulp.
[3] Analytical recoveries in this trial were in the range 47-78%. Residues, as in the other trials, are not corrected for recoveries.

Table 41. Pyriproxyfen and PYPAC residues in cotton seed resulting from supervised trials in the USA in 1994 and 1995 (Pensyl, 1996b). Double-underlined residues were from treatments according to GAP and were used to estimate an STMR and a maximum residue level.

Location year (variety)	Application					PHI, days	Pyriproxyfen, mg/kg	PYPAC, mg/kg[1]	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.				
AZ, 1994 (Delta Pine 50)	EC	0.10	0.053 +0.051	189 +196	2	29	<0.01	<0.01	NNR-0035 V-10946-A
AZ, 1994 (Delta Pine 50)	EC	0.19	0.10 +0.097	189 +196	2	29	0.02	0.01	NNR-0035 V-10946-A
CA, 1994 (Malla)	EC	0.097	0.040	240	2	29	0.02	<0.01	NNR-0035 V-10946-B
CA, 1994 (Malla)	EC	0.20	0.083	240	2	29	0.02	<0.01	NNR-0035 V-10946-B
TX, 1994 (MD51)	EC	0.10	0.053	186	2	29	<0.01	<0.01	NNR-0035 V-10946-C
TX, 1994 (MD51)	EC	0.20	0.11	187	2	29	<0.01	<0.01	NNR-0035 V-10946-C
GA, 1995 (DES 119)	EC	0.049 +2×0.074	0.034 +2×0.052	143	3	28	<0.01	<0.01	NNR-0035 V-11117-A
AR, 1995 (Stoneville 453)	EC	0.049 +2×0.074	0.035 +2×0.053	140	3	28	0.03	<0.01	NNR-0035 V-11117-B
TX, 1995 (Quickie)	EC	0.050 +2×0.074	0.035 +2×0.053	140	3	28	0.03	<0.01	NNR-0035 V-11117-C

Location year (variety)	Application					PHI, days	Pyriproxyfen, mg/kg	PYPAC, mg/kg[1]	Ref.
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.				
TX, 1995 (HS-200)	EC	0.050 +2×0.074	0.035 +2×0.053	140	3	28	0.01	<0.01	NNR-0035 V-11117-D
TX, 1995 (Paymoster 145)	EC	0.049 +2×0.075	0.036 +2×0.053	136 +140 +140	3	30	0.04	<0.01	NNR-0035 V-11117-E
TX, 1995 (Alltex Quickie)	EC	0.050 +2×0.075	0.035 +2×0.053	142 +142 +139	3	30	0.03	<0.01	NNR-0035 V-11117-F
TX, 1995 (MD 51)	EC	0.049 +2×0.075	0.035 +2×0.053	138 +144 +140	3	28	<0.01	<0.01	NNR-0035 V-11117-G
AZ, 1995 (Delta Pine 20)	EC	0.050 +2×0.074	0.035 +2×0.053	142 +141 +140	3	28	0.03	<0.01	NNR-0035 V-11117-H
LA, 1995 (DPL 51)	EC	0.050 +0.079 +0.075	0.035 +2×0.052	145 +152 +146	3	21 28 35	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	NNR-0035 V-11117-I
LA, 1995 (DPL 51)	EC	0.10 +0.16 +0.15	0.069 +2×0.10	144 +156 +145	3	28	<0.01	0.01[2]	NNR-0035 V-11117-I
CA, 1995 (Maxxa)	EC	0.049 +2×0.074	0.034 +2×0.052	144	3	21 28 35	<0.01 <0.01 <0.01	<0.01 <0.01 <0.01	NNR-0035 V-11117-J
CA, 1995 (Maxxa)	EC	0.10 +2×0.15	0.069 +2×0.10	143	3	28	0.02	<0.01	NNR-0035 V-11117-J
MS, 1995 (Delta Pine 50)	EC	0.050 +2×0.074	0.035 +2×0.053	141	3	28	<0.01	<0.01	NNR-0035 V-11117-K
AZ, 1995 (DP 5415)	EC	0.049 +2×0.072	0.035 +2×0.053	139	3	28	0.03	<0.01	NNR-0035 V-11117-M
AZ, 1995 (DP 5415)	EC	0.25 +2×0.36	0.17 +2×0.26	141 +138 +136	3	28	0.1	<0.01	NNR-0035 V-11117-N

[1] Unconjugated.
[2] <0.01 mg/kg on confirmatory GLC column.

Table 42. Pyriproxyfen and DPH-Pyr residues in cotton gin trash resulting from supervised trials in the USA 1995 (Pensyl, 1996b) and ginning of 20 kg lots of seed cotton. Residues are expressed on samples as received.

Location, year (variety)	Application					PHI, days	Pyriproxyfen, mg/kg	DPH-Pyr mg/kg	Moisture, %	Ref
	Form	kg ai/ha	kg ai/hl	water, l/ha	no.					
GA, 1995 (DES 119)	EC	0.049 +2×0.074	0.034 +2×0.052	143	3	28	0.45 c 0.04	0.04	21.8%	NNR-0035 V-11117-A
TX, 1995 (Quickie)	EC	0.050 +2×0.074	0.035 +2×0.053	140	3	28	0.68	0.03	29.8%	NNR-0035 V-11117-C
TX, 1995 (HS-200)	EC	0.050 +2×0.074	0.035 +2×0.053	140	3	28	0.35	0.08	30.3%	NNR-0035 V-11117-D
TX, 1995 (Paymoster 145)	EC	0.049 +2×0.075	0.036 +2×0.053	136 +140 +140	3	30	0.66	<0.01	21.8%	NNR-0035 V-11117-E
MS, 1995 (Delta Pine 50)	EC	0.050 +2×0.074	0.035 +2×0.053	141	3	28	1.4	0.06	14.9%	NNR-0035 V-11117-K
AZ, 1995 (DP 5415)	EC	0.049 +2×0.072	0.035 +2×0.053	139	3	28	2.3	0.07 c 0.07	13.8%	NNR-0035 V-11117-M

c: control

Groups of 3 lactating dairy cows (each weighing 400-620 kg and producing approximately 15 kg milk per day) were dosed with pyriproxyfen by gelatin capsule at 0.13, 0.38 or 1.17 mg/kg bw/day, equivalent to nominal feed levels of 3, 9 and 30 ppm in the diet on a dry weight basis for 28 days (Green, 1997). Milk was collected from two milkings each day for analysis. Each animal consumed 8.0 kg prepared feed, 16 kg alfalfa hay cubes and 2 kg bailed hay as the basal daily feed (Helsten, 1996). The animals were slaughtered on day 29. Muscle samples were composites of hind quarter, pectoral and abductor muscle in equal proportions, and fat samples of perirenal, abdominal and subcutaneous fat in equal proportions. Milk and tissues were analysed for pyriproxyfen and the major metabolites identified in the metabolism studies (Tables 43 and 44). Analyses for the metabolites included a hydrolysis step, so the recorded residues include both free and conjugated compounds. LODs were generally 0.01 mg/kg, but sometimes 0.02 mg/kg because of interference. In the studies of goat metabolism free and conjugated 4'-OH-Pyr was generally the main identified metabolite; other metabolites would not be expected to be detectable in its absence. In the kidneys of the cows in the 30 ppm group however, 2,5-OH-Py was detected when 4'-OH-Pyr was not.

The residues in the milk from the 30 ppm feeding group are shown in Table 43. Milk samples up to day 14 from the other two groups were also analysed, but residues were not detected. Residues of pyriproxyfen, but not the metabolites, were detected in the cream of milk from the 30 ppm group taken on day 24, implying that pyriproxyfen is fat-soluble. Pyriproxyfen was not detected (<0.01 mg/kg) in the cream of milk from the 9 ppm group taken on day 24.

In the tissues pyriproxyfen itself was detected only in the fat, again confirming its classification as a fat-soluble compound. Mean residues of 0.058 mg/kg in the 30 ppm group and 0.018 mg/kg in the 9 ppm group suggested that residues would be proportional to the doses.

Milk samples were extracted and analysed within 5 days of collection, so the residues would be stable. Pyriproxyfen residues in the tissues were determined within 9-23 days after sampling, and had been shown to be stable for this period by the storage stability studies. POP residues in the liver

and kidneys were extracted 49 and 67 days after sampling. Storage stability trials showed that the sulfate conjugate of POP would decrease by about 30% in 66 days, so the results could be accepted. Storage periods for residues of 4'-OH-Pyr in the tissues were 45-70 days, shorter than the demonstrated periods of stability. Samples were stored for 109-113 days before analysis for 2,5-OH-Py. Stability trials showed considerable losses of free 2,5-OH-Py by this time and no data were available for its conjugates. Studies of the storage stability of free POP and 4'-OH-Pyr in the liver were abandoned when significant degradation was observed within about 2 months.

Table 43. Residues of pyriproxyfen and metabolites in milk from dairy cows dosed with pyriproxyfen at the equivalent of a nominal feed level of 30 ppm dry weight for 28 days (Green, 1997). Metabolite residues include free and conjugated compounds.

Day	Sample	Residues, mg/kg, in milk from 3 cows			
		pyriproxyfen	POP	4'-OH-Pyr	2,5-OH-Py
1	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
2	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
4	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
7	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
10	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
14	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
17	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
21	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
24	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
28	whole milk	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
24	skimmed milk	<0.01 (3)	<0.01 (3)	<0.02 (3)	<0.01 (3)
24	cream	0.012 0.015 0.014	<0.02 (3)	<0.02 (3)	<0.02 (3)

Table 44. Residues of pyriproxyfen and metabolites in the tissues from dairy cows dosed with pyriproxyfen equivalent to nominal feed levels of 3, 9 or 30 ppm dry weight for 28 days (Green, 1997). Metabolite residues include free and conjugated compounds.

Sample	Dose groups, ppm	Residues, mg/kg, from 3 cows			
		pyriproxyfen	POP	4'-OH-Pyr	2,5-OH-Py
Muscle	30	<0.01 (3)		<0.01 (3)	
Liver	30	<0.01 (3)	<0.01 (3)	<0.01 (3)	<0.01 (3)
Kidneys	9	<0.01 (3)			<0.01 (3)
Kidneys	30	<0.01 (3)	<0.02 (3)	<0.01 (3)	0.017 0.014 0.016
Fat	3	<0.01 (3)			
Fat	9	0.025 0.011 0.019			
Fat	30	0.058 0.046 0.072		<0.01 (3)	

Residues in animal commodities

The Meeting estimated the dietary burden (Table 45) of pyriproxyfen for beef and dairy cattle from the diets in Appendix IX of the FAO Manual, the recommended MRLs for cotton gin trash and cotton seed, and the maximum residue level for cotton seed meal derived from the recommended MRL for cotton seed and the relevant processing factor (0.1). These three commodities from cotton were the only feed items considered. The dietary burden for both beef and dairy cattle is equivalent to 1.1 ppm pyriproxyfen and is suitable for estimating maximum residue levels for meat, offal and milk.

A similar calculation from the STMR levels for the feed commodities gives a dietary burden of 0.21 ppm pyriproxyfen, which is suitable for estimating STMRs for animal commodities.

Table 45. Estimated dietary burden of pyriproxyfen for beef and dairy cattle calculated from recommended MRLs, STMRs and standard animal diets. DM is dry matter. MRL/DM is MRL expressed on the dry matter. The residues in cotton gin trash are already expressed on a dry matter basis, so no adjustment is needed.

Commodity	MRL, mg/kg	Processing factor[1]	DM, %	MRL/DM, mg/kg	%, of diet		Pyriproxifen in diet, ppm	
					Beef	Dairy	Beef	Dairy
Cotton gin trash	5		100	**5.00**	20	20	1.00	1.00
Cotton seed (undelinted)	0.05		88	**0.057**	25	25	0.01	0.01
Cotton seed meal	0.005	0.1	89	**0.006**				
							1.0	**1.0**
	STMR			STMR/DM				
Cotton gin trash	0.91		100	**0.91**	20	20	0.18	0.18
Cotton seed (undelinted)	0.01		88	**0.011**	25	25	0.00	0.00
Cotton seed meal	0.001	0.1	89	**0.001**				
							0.18	**0.18**

[1] The processing factor for cotton seed meal in a processing trial was 0 (<0.1), taken as 0.1 for the calculation. The cotton seed meal "MRL" of 0.005 mg/kg is calculated from the recommended MRL for cotton seed and the processing factor.

Interpretation of residue trials

Table 46. Interpretation table for pyriproxyfen residues in citrus fruits, cotton seed and cotton gin trash. GAP and trial conditions are compared for treatments considered valid for the estimation of maximum residue levels and STMRs.

Crop	Country	Use pattern				Trial	Pyriproxyfen, mg/kg
		kg ai/ha	kg ai/hl	No of appl	PHI, days[1]		
CITRUS FRUIT							
Citrus GAP	Israel	0.25-0.40	0.01		GS		
Grapefruit trial	Israel	0.35	0.01	1	137	1628/1	0.03 pulp <0.01
Grapefruit trial	Israel	0.4	0.01	1	130	1628/1	0.04 pulp <0.01
Grapefruit trial	Israel	0.3	0.01	1	121	1628/1	0.08 pulp <0.01
Grapefruit trial	Israel	0.4	0.01	1	126	1628/1	0.03 pulp <0.01
Grapefruit trial	Israel	0.35	0.01	1	124	1628/1	0.03 pulp <0.01
Citrus GAP	SA		0.0030	3	90		
Mandarin trial	SA	0.36	0.003	2	90	IK30196/97	0.02 pulp <0.01
Orange trial	SA	0.36	0.003	2	90	IK30296/97	0.02 pulp <0.01
Orange trial	SA	0.36	0.003	2	120 (90)	311P130	0.05 pulp <0.01
Orange trial	SA	0.36	0.003	2	120 (90)	311P130	0.06 pulp<0.01
Citrus GAP	Spain		0.0025-0.0075	2	30		
Mandarin trial	Spain	0.08	0.005	1	31	S/SP/E/91971	0.069
Mandarin trial	Spain		0.005	1	31	S/SP/M/92163	0.20
Mandarin trial	Spain		0.005	1	31	S/SP/M/92160	0.33
Mandarin trial	Spain	0.23	0.007	1	45 (30)	R10.A.97.027	0.10
Orange trial	Spain	0.08	0.005	1	31	S/SP/E/91972	0.12
Orange trial	Spain		0.005	1	31	S/SP/M/92161	0.25
Orange trial	Spain		0.005	1	45 (31)	S/SP/M/92162	0.25
Orange trial	Spain	0.23	0.007	1	45 (30)	R10.A.97.025	0.08

Crop	Country	Use pattern				Trial	Pyriproxyfen, mg/kg
		kg ai/ha	kg ai/hl	No of appl	PHI, days[1]		
Orange trial	Italy	0.07	0.007	1	60 (28)	Pyriproxyfen-IT-1996-1	0.06 pulp <0.01
COTTON SEED							
Cotton GAP	USA	0.059-0.075		1	28		
Cotton seed trial	USA	0.10	0.053 +0.051	2	29	V-10946-A	<0.01
Cotton seed trial	USA	0.097	0.040	2	29	V-10946-B	0.02
Cotton seed trial	USA	0.10	0.053	2	29	V-10946-C	<0.01
Cotton seed trial	USA	0.049 +2×0.074	0.034 +2×0.052	3	28	V-11117-A	<0.01
Cotton seed trial	USA	0.049 +2×0.074	0.035 +2×0.053	3	28	V-11117-B	0.03
Cotton seed trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-C	0.03
Cotton seed trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-D	0.01
Cotton seed trial	USA	0.049 +2×0.075	0.036 +2×0.053	3	30	V-11117-E	0.04
Cotton seed trial	USA	0.050 +2×0.075	0.035 +2×0.053	3	30	V-11117-F	0.03
Cotton seed trial	USA	0.049 +2×0.075	0.035 +2×0.053	3	28	V-11117-G	<0.01
Cotton seed trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-H	0.03
Cotton seed trial	USA	0.050 +0.079 +0.075	0.035 +2×0.052	3	28	V-11117-I	<0.01
Cotton seed trial	USA	0.049 +2×0.074	0.034 +2×0.052	3	28	V-11117-J	<0.01
Cotton seed trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-K	<0.01
Cotton seed trial	USA	0.049 +2×0.072	0.035 +2×0.053	3	28	V-11117-M	0.03
COTTON GIN TRASH							
Cotton GAP	USA	0.059-0.075		1	28		
Cotton gin trash trial	USA	0.049 +2×0.074	0.034 +2×0.052	3	28	V-11117-A	0.58 [2]
Cotton gin trash trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-C	0.97 [2]
Cotton gin trash trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-D	0.50 [2]
Cotton gin trash trial	USA	0.049 +2×0.075	0.036 +2×0.053	3	30	V-11117-E	0.84 [2]
Cotton gin trash trial	USA	0.050 +2×0.074	0.035 +2×0.053	3	28	V-11117-K	1.65 [2]
Cotton gin trash trial	USA	0.049 +2×0.072	0.035 +2×0.053	3	28	V-11117-M	2.67 [2]

[1] A shorter PHI in parentheses is the GAP PHI, but the residue was higher at the longer PHI and was used for the evaluation.
[2] expressed on a dry weight basis

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information.

In processing

Cotton was treated three times with pyriproxyfen at an exaggerated rate and harvested 28 days after the final application for processing (Pensyl, 1996b). The residue trial is included in Table 41 (trial V-11117-N). The processing procedure is shown in Figure 6. Pyriproxyfen residues of 0.10 mg/kg in cotton seed produced residues of 0.02 mg/kg in the crude and refined oil, but no residues (<0.01 mg/kg) in the meal (Table 47). PYPAC residues were below the LOD (0.01 mg/kg) in both the raw and processed commodities.

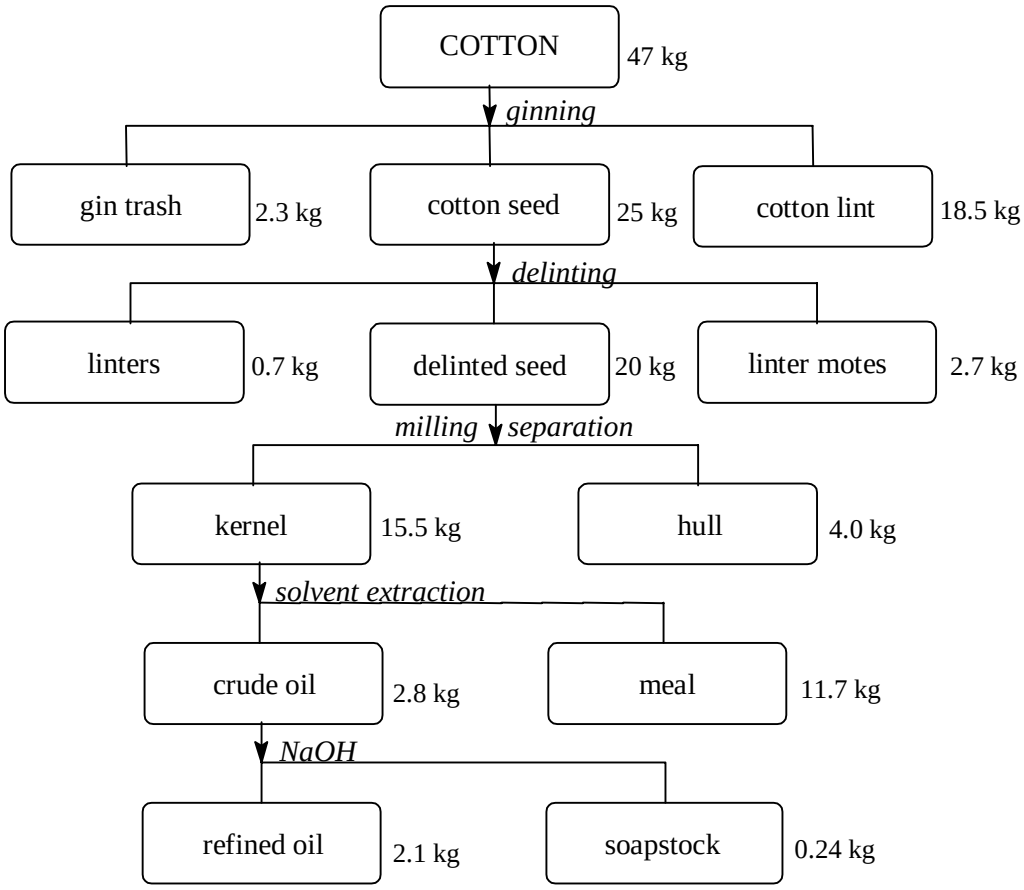


Figure 6. Cotton seed processing (Pensyl, 1996b).

Table 47. Residues in cotton seed and its processed fractions from cotton treated at a fivefold rate, 0.25 + 0.37 + 0.37 kg ai/ha, and harvested 28 days after the final application in the USA (Pensyl, 1996b).

Commodity	Pyriproxyfen, mg/kg	PYPAC, mg/kg
Cotton seed	0.10	<0.01
Solvent-extracted meal	<0.01	<0.01
Cotton hulls	<0.01	<0.01
Crude oil	0.02	<0.01

Commodity	Pyriproxyfen, mg/kg	PYPAC, mg/kg
Refined oil	0.02	<0.01

Residues in the edible portion of food commodities

Pyriproxyfen residues were not detected (<0.01 mg/kg) in the edible pulp in 24 citrus trials. The calculated factors for transfer to the pulp are based on the level in the whole fruit and the LOD so that the real factors, if residues enter the pulp, are somewhat lower. The mean and minimum factors were 0.33 and 0.09 respectively. The mean factor was used in the estimation of the STMR for citrus fruits.

In a processing trial on cotton seed the processing factor for both crude and refined cotton seed oil was 0.2. The Meeting applied this factor to the STMR for cotton seed to calculate the STMR for cotton seed oils.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

The Meeting received information from The Netherlands on pyriproxyfen residues in food in commerce in 1997. The residues were below the LOD (0.02 mg/kg) in 172 of the 175 tomato samples analysed and did not exceed the MRL (0.1 mg/kg) in the remaining 3 samples.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware that the following national MRLs had been established.

Country	MRL, mg/kg	Commodity
Brazil	0.1	bean
Brazil	0.1	citrus fruits
Brazil	0.5	tomato
Netherlands [1]	0.1	solanaceae
Netherlands	0.02*	other food commodities
Spain	0.5	citrus fruits
USA	0.05	cotton seed
USA	2	gin trash

[1] Residue definition: parent compound, expressed as pyriproxyfen

APPRAISAL

Pyriproxyfen is an insect growth regulator with insecticidal activity against public health insect pests: houseflies, mosquitoes and cockroaches. In agriculture and horticulture pyriproxyfen has registered uses for the control of scale, whitefly, bollworm, jassids, aphids and cutworms.

The Meeting received extensive information on pyriproxyfen metabolism and environmental fate, methods of residue analysis, freezer storage stability, national registered use patterns, supervised trials, farm animal feeding studies, fate of residues in processing and national MRLs.

Animal metabolism

When rats were dosed orally with [^{14}C]pyriproxyfen excretion of the ^{14}C was rapid, accounting for 88-96% in 2 days. ^{14}C levels were higher in the fat than in other tissues and slightly more persistent. The

estimated biological half-life for ^{14}C depletion in fat was 36 hours. The main metabolite in the faeces was 4-(4-hydroxyphenoxy)phenyl (*RS*)-2-(2-pyridyloxy)propyl ether (4'-OH-Pyr).

When lactating goats were dosed with [^{14}C]pyriproxyfen, labelled in either the phenyl or the pyridyl ring, at the equivalent of 10 ppm in the feed for 5 consecutive days most of the dose was accounted for by residues in the excreta and the contents of the GI tract. Pyriproxyfen (0.003-0.009 mg/kg) was a minor component of the milk residue (3-15%) with the main metabolite 4'-OH-Pyr sulfate constituting about 30-50%. Parent pyriproxyfen (0.014-0.050 mg/kg) was the main residue in fat with essentially the same levels in omental and perirenal fat. Pyriproxyfen was the main residue in muscle but levels were very low. It was a very minor component of the residues in the kidneys and liver. The main identified residue in the liver was 4'-OH-Pyr sulfate, while in the kidneys the main identified residues were 4'-OH-Pyr sulfate and 4-phenoxyphenyl sulfate (POP sulfate).

Approximately 90% of the dose appeared in the excreta of laying hens dosed with [^{14}C]pyriproxyfen labelled in either the phenyl or pyridyl ring for 8 consecutive days at the equivalent of 10 ppm in the feed. The main identified residues in the excreta were 4'-OH-Pyr and (*RS*)-2-(2-pyridyloxy)propionic acid (PYPAC). The residues were very low in the egg whites and reached a plateau in the yolks in about 6 days in one experiment and had almost reached a plateau in the other. Parent pyriproxyfen (up to 0.17 mg/kg) was the main residue in egg yolk. The residues in muscle were below those in other tissues and pyriproxyfen was the main component of the residue. The residues in fat were much higher than in muscle, suggesting a fat-soluble compound, and pyriproxyfen was the main residue. Levels of pyriproxyfen in abdominal fat (0.79 and 0.92 mg/kg) were much higher than in the skin + fat (0.17 and 0.13 mg/kg). Pyriproxyfen was a minor component of the liver residue with 4'-OH- Pyr sulfate the main identified metabolite.

The Meeting concluded that the animal metabolism studies were marginally acceptable where data on freezer storage stability were available, but not for residues in milk and eggs. Summary information on the storage stability of pyriproxyfen and its metabolites in goat milk and egg yolk were provided at a late stage of the Meeting, which suggested that the residues were stable during freezer storage. The full report should be evaluated the next time pyriproxyfen is reviewed.

Plant metabolism

Pyriproxyfen accounted for most of the residue in apples when trees were treated with labelled pyriproxyfen soon after petal fall and twice more at 60 and 40 days before harvest. A surface wash accounted for only 1.5-2.6% of the total apple residue. Pyriproxyfen was not detectable in apple juice, where the main identified residue was (*RS*)-2-(2-pyridyloxy)propyl alcohol (PYPA). Pyriproxyfen was the main component of the residue in apple pomace.

When tomato plants were treated 3 times with ^{14}C-labelled pyriproxyfen 35, 21 and 7 days before harvest, a surface wash of the harvested fruit with acetonitrile accounted for 1.8-3.3% of the residues in the tomatoes. Pyriproxyfen was not detectable in the tomato juice, where the identified metabolites were PYPA, PYPAC and 2-hydroxypyridine (2-OH-PY) in free and conjugated form. Parent pyriproxyfen accounted for most of the residue in whole tomatoes and tomato pomace.

Pyriproxyfen was the main residue component in gin trash from cotton plants treated twice, 43 and 28 days before harvest, with ^{14}C-labelled pyriproxyfen. Levels of ^{14}C were much lower in the cotton seed than in the gin trash suggesting little, if any, translocation of the residue from leaf to seed. The main identified residue in cotton seed was free and conjugated PYPAC with pyriproxyfen constituting only 3.9% and 0.6% of the residue. Approximately half of the residue in cotton seed was unextractable and was associated with the protein, carbohydrate and lignin fractions.

Metabolic pathways in plants and animals are very similar.

Environmental fate in soil

Labelled pyriproxyfen disappeared rapidly in the first few days during aerobic degradation in soil but then more slowly, with an estimated half-life of 28 days from days 7 to 30 of the study. Half-lives for mineralization were 68 and 139 days for the pyridyl label and phenyl label respectively. The main identified residue was 4'-OH-Pyr, but it did not exceed 5% of the dose.

In a second study of aerobic soil degradation the half-lives for pyriproxyfen were 8.2 days for days 1-14 and 20 days for days 14-91, while mineralization half-lives were 82 and 112 days for the pyridyl and phenyl label respectively. PYPAC was the main identified product, reaching 15% of the dose with levels exceeding those of pyriproxyfen after day 28. In a further aerobic study for 6 months the results were generally consistent with the previous ones but mineralization was found to be very slow with estimated half-lives of 330 and 850 days.

The leaching of [^{14}C]pyriproxyfen was determined with columns of silt and sandy loam soils. Most of the ^{14}C (89% and 84%) remained in the treated soil at the top of the column. Pyriproxyfen is unlikely to be leached, and degradation products become substantially bound in the soil organic matter.

The leaching of residues aged by aerobic soil incubation for 9 days was also determined. Most of the residue (86-88.5%) remained in the applied soil at the top of the leaching column. PYPAC was mobile and constituted 6.5 of the 7.6% of the applied dose which appeared in the leachate.

After a series of adsorption-desorption studies, pyriproxyfen was rated as essentially immobile and unlikely to be leached from most agricultural soils. 4'-OH-Pyr was rated as having slight to low mobility in most agricultural soils or a slight chance of leaching. On the basis of its adsorption values, PYPAC was rated as having high or very high mobility with a high potential to be leached into ground water. Whether the potential to be leached is realized will depend on the persistence of PYPAC in the soil and the prevailing field conditions.

Pyriproxyfen disappeared more quickly from irradiated soil than from dark controls and produced polar and unextractable residues. However, the rate of photolysis was not so much faster than that of soil degradation as to suggest that photolysis would be a main mechanism of environmental degradation.

In a confined rotational crop study, lettuce, radishes and wheat seed were sown in a soil treated 30 days previously with [^{14}C]pyriproxyfen at 0.20 kg ai/ha. Levels of ^{14}C were negligible in lettuce leaves, radish roots and leaves and wheat forage from crops grown to maturity. The ^{14}C in wheat grain, straw and chaff was unextractable and found to be biochemically incorporated into proteins and carbohydrates. The residues of pyriproxyfen and its immediate metabolites or degradation products would not be expected above negligible levels in rotational crops.

In two field dissipation studies pyriproxyfen residues did not migrate down the soil profile and the disappearance half-lives in the top soil segment were 3.5 and 16 days. PYPAC was detected in only one sample, in the top segment of the soil. 4'-OH-Pyr was detected sporadically at concentrations close to the LOD, but the incidence could not be interpreted as evidence of systematic persistence or mobility down the soil profile.

Environmental fate in water-sediment systems

Pyriproxyfen disappeared from aerobic lake water-sediment systems with half-lives of 16 and 21 days. Pyriproxyfen was the main residue in the sediment during the 1-month studies, and 4'-OH-Pyr

accounted for 7.5% and 9.5% of the dose after 7 days. PYPAC was the main residue in the water phase after 12 days and accounted for 34% of the dose on day 21.

Pyriproxyfen was the main residue throughout 1-year studies of anaerobic lake water-sediment systems and most of the residue was in the sediment. PYPAC accounted for 16% of the dose after 1 year and, because of its water solubility, it was mainly in the aqueous phase. Mineralization was negligible. Pyriproxyfen appeared to be degraded slowly for the first 6 months and subsequently more quickly.

In a photolysis study, pyriproxyfen was exposed to sunlight in sterilized distilled water and sterilized lake water. The estimated photolytic half-lives were 17.5 and 21 days respectively. A theoretical half-life of 16 days was calculated for 40° N latitude. The main photoproducts were PYPA and CO_2 accounting for 16-30% and 11-29% of the initial ^{14}C respectively.

In a laboratory photolysis study pyriproxyfen in water was subjected to light from a xenon lamp with a filter to restrict light below 290 nm for 14 days. Estimated half-lives for photolytic disappearance were 6.4 and 3.7 days. The main photoproduct was PYPA. Negligible amounts of CO_2 were produced.

Analytical methods

Methods of analysis for pyriproxyfen and its metabolites in crops, processed commodities, animal commodities, soil and water were reported.

In a typical method pyriproxyfen residues are extracted with acetone, the extract is diluted with aqueous sodium chloride, and the residues are partitioned into dichloromethane. Column chromatography is used for clean-up and the residues are determined by GLC with an NPD. The LOD is usually about 0.02 mg/kg.

PYPAC remains in the aqueous phase during the extraction with dichloromethane. After acidification it is extracted into an organic phase such as ethyl acetate. PYPAC is methylated, cleaned up on a silica gel column and determined by GLC with an NPD. The LOD is about 0.02 mg/kg. Care must be exercised not to lose methyl PYPAC during the evaporation of its solutions because it is volatile.

An acid hydrolysis step is introduced into methods for POP (4-phenoxyphenol) and 4'-OH-Pyr in animal commodities to release conjugates. After clean-up, these metabolites are determined by HPLC with UV detection. 2,5-OH-Py (2,5-dihydroxypyridine) may be determined by HPLC with fluorescence detection.

Analytical methods for soils begin with various extractions and then follow the methods for crop residues. Typical LODs for pyriproxyfen and its degradation products in soils are 0.02 mg/kg. The validated LOD for a straightforward GLC method for pyriproxyfen in aquarium water was 1 µg/l.

Adequate recoveries of pyriproxyfen were achieved from apples and cotton seed fortified at 0.05 and 0.5 mg/kg with an FDA multi-residue method. PYPAC was not recovered from the Florisil column in this method.

Stability of pesticide residues in stored analytical samples

Pyriproxyfen and its metabolites were generally stable in crop and soil samples during freezer storage (-18°C to -20°C) for the periods tested.

Pyriproxyfen and some metabolites were of doubtful stability in animal commodities when stored for long periods.

Pyriproxyfen was stable in tomato homogenate for 12 months, cotton seed for 13 months, gin trash for 8 months, and soils for 7 months.

PYPAC was stable in cotton seed for 13 months and soils for 7 months. 4'-OH-Pyr was stable in fat for 14 weeks, muscle tissue for 10 weeks and one soil for 5 months, but decreased by 70% in another soil in 107 days. 4'-OH-Pyr sulfate was stable in cow liver for 8 weeks, but POP sulfate in cow liver decreased by about 30% in 72 days and 2,5-OH-Py in kidneys decreased by 85% in 70 days.

Definition of the residue

The main residue in the metabolism studies on plant commodities was pyriproxyfen itself. In cotton seed the levels of free + conjugated PYPAC and PYPA exceeded that of pyriproxyfen, which was very low, probably because the metabolites were translocated more readily. PYPAC in cotton seed in the metabolism study was about 60% free and 40% conjugated, but in the trials on cotton free PYPAC was generally undetected and lower than pyriproxyfen in the seed.

The residue can be defined as pyriproxyfen for enforcement in crops.

In animal commodities the composition of the residue varies in different tissues. Pyriproxyfen itself is fat-soluble (log P_{OW} 5.37) so it predominates in fat. In muscle all the residues are very low, but pyriproxyfen is again the main component. In milk and liver 4'-OH-Pyr with its sulfate conjugate are the main residues, while in kidneys POP is the main residue with 4'-OH-Pyr also a significant component. Pyriproxyfen predominates in eggs.

The feeding study on dairy cows suggests that the residues in milk and tissues will generally be undetectable or very low whatever the residue definition, except pyriproxyfen itself in fat and the fat of milk at the higher dietary burdens. The Meeting agreed it would be unpractical to define the residue to include metabolites and their conjugates in liver and kidneys for undetectable residues; it would be a pointless additional analytical expense.

Pyriproxyfen is also a suitable definition of the residue for dietary intake estimates.

Proposed definition of the residue (for compliance with MRLs and for the estimation of dietary intake): pyriproxyfen.

The residue is fat-soluble.

Residues resulting from supervised trials

Citrus fruits. Pyriproxyfen is registered for use on citrus fruit in Israel at 0.01 kg ai/hl with the final application at the end of May for varieties picked until the end of December and the end of June for those picked after the end of December. Five trials on grapefruit in substantial accord with Israeli GAP (sprayed in early June instead of the end of May) gave pyriproxyfen residues in the whole fruit of 0.03 (3), 0.04 and 0.08 mg/kg. The residues in the pulp were below the LOD (0.01 mg/kg).

South African GAP permits 3 applications of pyriproxyfen at a spray concentration of 0.0030 kg ai/hl with harvest 90 days after the final application. One trial on mandarins and 3 on oranges substantially complying with GAP (2 applications instead of 3) produced residues of 0.02 mg/kg in the mandarins and 0.02, 0.05 and 0.06 mg/kg in the oranges.

In Spain pyriproxyfen may be applied twice to citrus fruit at 0.0025-0.0075 kg ai/hl with harvest 30 days after the final application. Four trials on mandarins with 1 application of 0.005 and 0.007 kg ai/hl and harvest after 31 and 45 days (the residue at 45 days exceeded the residue at 30 days) were acceptably close to GAP and produced residues of 0.069, 0.10, 0.20 and 0.33 mg/kg. Recoveries in trial NNR-21-0018 were low and the results should be adjusted for the recovery (62.5%). The values 0.20 and 0.33, on adjustment, become 0.32 and 0.53 mg/kg. The residues in oranges from 4 trials in Spain and 1 in Italy substantially in line with Spanish GAP produced residues of 0.06, 0.08, 0.12, 0.25 and 0.25 mg/kg.

In summary, pyriproxyfen residues in the 18 trials according to GAP were Italy oranges 0.06 mg/kg, Israel grapefruit 0.03 3, 0.04, 0.08 mg/kg, South Africa mandarins 0.02 mg/kg, oranges 0.02, 0.05 and 0.06 mg/kg, and Spain mandarins 0.069, 0.10, 0.32, 0.53; oranges 0.08, 0.12, 0.25, 0.25 mg/kg.

The Meeting agreed that the residues arising from the Spanish GAP with the 30 days PHI seemed to be a different population from the residues from South African and Israeli GAP and that the higher population would be used for the estimation of an STMR and maximum residue level. The residues in rank order (median underlined) from the trials according to Spanish GAP were 0.06, 0.069, 0.08, 0.1, <u>0.12</u>, 0.25, 0.25, 0.32 and 0.53 mg/kg.

Because data were available for grapefruit, mandarins and oranges the Meeting agreed that an MRL for citrus fruits was appropriate. The Meeting estimated a maximum residue level for pyriproxyfen on citrus fruits of 1 mg/kg.

Pyriproxyfen residues were not detected (<0.01 mg/kg) in the edible pulp in 24 samples analysed during the citrus trials, but many of the samples did not reflect GAP conditions so the results could not be used directly, and the residues in the whole fruit only just exceeded the LOD. The mean ratio of the residue in the pulp to that in the whole fruit for the 3 samples with the highest residues in the whole fruit was 0.11, which is artificially high because it is largely an artefact of the LOD. The Meeting applied this factor to the median residue from the 9 relevant trials (0.12 mg/kg) to estimate an STMR of 0.013 mg/kg for pyriproxyfen in citrus fruits.

<u>Cotton seed</u>. Pyriproxyfen may be applied to cotton at 0.059-0.075 kg ai/ha with the crop harvested 28 days after the single application. In a series of trials in the USA in 1994 and 1995 pyriproxyfen was applied 2 or 3 times to cotton with the final application in the range 0.072-0.10 kg ai/ha, which was considered to comply with GAP for residue purposes. The pyriproxyfen residues in cotton seed in rank order (median underlined) in the 15 trials were <0.01 (7), <u>0.01</u>, 0.02, 0.03 (5) and 0.04 mg/kg.

The Meeting estimated a maximum residue level of 0.05 mg/kg and an STMR of 0.01 mg/kg for pyriproxyfen in cotton seed.

<u>Cotton gin trash</u>. In 6 of the US cotton trials in 1995 seed cotton (20 kg) was ginned to produce cotton seed and gin trash and pyriproxyfen residues were measured on the gin trash. The residues, expressed on a dry weight basis, in rank order (median underlined) were 0.50, 0.58, <u>0.84</u>, <u>0.97</u>, 1.7 and 2.7 mg/kg.

The Meeting estimated a maximum residue level and an STMR for pyriproxyfen in cotton gin trash of 5 and 0.91 mg/kg respectively.

<u>Feeding trials</u>

Pyriproxyfen and metabolites identified in the metabolism study were determined in the milk and tissues from dairy cows dosed for 28 days with pyriproxyfen at 0.13, 0.38 and 1.17 mg/kg bw/day, equivalent to 3, 9 and 30 ppm dry weight in the diet. In the 30 ppm group pyriproxyfen residues were not detected (<0.01 mg/kg) in whole milk, muscle, liver or kidney, but were present in cream from

day 24 milk (0.012-0.015 mg/kg) and in body fat (0.046-0.072 mg/kg). In the 9 ppm feeding group, pyriproxyfen residues were not detected in milk and kidney, but were present in body fat at 0.011-0.025 mg/kg. In the 3 ppm feeding group, pyriproxyfen residues were not detected (<0.01 mg/kg) in body fat, whole milk or the cream of day 24 milk.

The residues in the body fat in the 30 ppm group (mean 0.058 mg/kg) and the 9 ppm group (mean 0.018 mg/kg) were roughly proportional to the doses.

Residues in animal commodities

The dietary burden for estimating maximum residue levels for animal commodities for beef and dairy cattle is 1.0 ppm pyriproxyfen, calculated from the maximum residue levels estimated for cotton gin trash and cotton seed. This level is sufficiently close to be evaluated against the 3 ppm feeding level which did not produce pyriproxyfen residues above the LOD (0.01 mg/kg) in the animal commodities.

The dietary burden for estimating STMRs for products of beef and dairy cattle is 0.18 ppm pyriproxyfen, calculated from the STMRs estimated for cotton gin trash and cotton seed.

The Meeting estimated maximum residue levels of 0.01* mg/kg for cattle meat (fat), cattle edible offal and cattle milk. The Meeting noted that residues resulting from feeding dairy cows at 10 ppm were quite similar to those found in the 10 ppm goat metabolism study and agreed that the estimated maximum residue levels could be extended to milks and to goat meat (fat) and goat edible offal. However, the estimated maximum residue level for milks cannot be recommended for use as an MRL because the stability of pyriproxyfen and its metabolites in goat milk is yet to be confirmed.

The residues were below the LOD in the muscle, liver and kidneys at feeding levels of 3, 9 and 30 ppm. Residues of pyriproxyfen were detected in the fat at the 9 and 30 ppm feeding levels and in the fat of milk at the 30 ppm feeding level. The Meeting noted that the dietary burden of 0.18 ppm was much lower than the lowest feeding level and as an approximation assumed proportionality between likely tissue levels and dietary intake.

STMR (animal commodity) = LOD × (STMR dietary burden) ÷ (feeding level)

STMR for meat = 0.01 × 0.18 ÷ 30 = 0.00006 mg/kg (no detections at 30 ppm feeding level)

The same calculation applies for liver, kidneys and milk. The Meeting agreed that the calculated STMRs were low enough to be treated as effectively zero. The Meeting estimated STMR levels of 0 for cattle meat, goat meat, cattle edible offal, goat edible offal and milks, but could not recommend the use of the STMR for milks until the maximum residue level estimated for milks can be recommended for use as anMRL.

Processing

In a cotton seed processing trial pyriproxyfen residues of 0.1 mg/kg in cotton seed produced residues of 0.02 mg/kg in both crude and refined oil and no detectable residues in the meal (<0.01 mg/kg). The estimated processing factors for crude oil and refined oil are therefore 0.2 and the processing factor for cotton seed meal is 0 (<0.1).

The Meeting applied the processing factors to the maximum residue level and STMR for cotton seed to produce estimated maximum residue levels of 0.01 mg/kg and STMRs of 0.002 mg/kg for crude and edible cotton seed oil, and an estimated STMR for cotton seed meal of 0.001 mg/kg.

Similarly, the processing factor 0.2 applied to the maximum trials residue value for cotton seed (0.04 mg/kg) produced maximum trials residue values of 0.008 mg/kg for crude and edible cotton seed oils.

RECOMMENDATIONS

On the basis of the data from supervised trials the Meeting estimated the maximum residue levels and STMRs listed below. The maximum residue levels are recommended for use as MRLs.

Definition of the residue (for compliance with MRLs and for estimation of dietary intake): pyriproxyfen.

The residue is fat-soluble.

Commodity		MRL, mg/kg	STMR, mg/kg
CCN	Name		
MM 0812	Cattle meat	0.01* (fat)	0
MO 0812	Cattle, Edible offal of	0.01*	0
FC 0001	Citrus fruits	1	0.013
	Cotton gin trash	5	0.91
SO 0691	Cotton seed	0.05	0.01
	Cotton seed meal		0.001
OC 0691	Cotton seed oil, crude	0.01	0.002
OR 0691	Cotton seed oil, edible	0.01	0.002
MM 0814	Goat meat	0.01* (fat)	0
MO 0814	Goat, Edible offal of	0.01*	0

FURTHER WORK OR INFORMATION

Desirable

1. Information on the fate of pyriproxyfen during the processing of oranges. At a late stage of the Meeting information on an orange processing study was provided. It should be evaluated the next time pyriproxyfen is reviewed.

2. Information on the freezer storage stability of pyriproxyfen and the main metabolites in milk and eggs is necessary to validate the data from the metabolism studies. At a late stage of the Meeting a

summary report on the freezer storage stability of residues in goat milk and egg yolk was provided. The full report should be evaluated the next time pyriproxyfen is reviewed.

DIETARY RISK ASSESSMENT

Chronic intake

Pyriproxyfen is a new compound and maximum residue and STMR levels were estimated for citrus fruits, cotton seed, animal commodities and some processed commodities. The dietary intake of pyriproxyfen is presented in Annex III.

International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on estimated STMRs, were effectively 0% of the ADI. The Meeting concluded that the intake of residues of pyriproxyfen resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern

Acute intake

The Meeting concluded that an acute RfD for pyriproxyfen is unnecessary. This conclusion was based on a determination that the pesticide is unlikely to present an acute toxicological hazard and residues are therefore unlikely to present an acute risk to consumers.

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TEBUFENOZIDE

EXPLANATION

The insecticide tebufenozide was first evaluated by the 1996 JMPR when an ADI was allocated and MRLs were recommended for pome fruit, grapes, walnut and husked rice. Residue trials on kiwifruit in accordance with revised New Zealand GAP were reviewed by the 1997 JMPR and an MRL was recommended.

At the 31st (1999) Session of the CCPR the delegation of Germany stated that the German GAP for grapes and pome fruit was no longer pending (ALINORM 99/24A, para 103). Information on current GAP in Germany was submitted to allow re-evaluation of tebufenozide residues in grapes and pome fruit.

USE PATTERN

Registered German GAP allows application of tebufenozide to grapes and pome fruit to control moths 2-4 times at intervals of 14 days. Details are shown in Table 1.

Table 1. Registered uses of tebufenozide in Germany.

Crop	Form.	Application					PHI, days
		Method	Rate, kg ai/ha	Water, l/ha	Spray conc., kg ai/hl	No.	
Pome fruit	SC	Foliar spraying or atomizing spraying	0.18[1]	1500[1]	0.012[1]	3	14
Wine grapes	SC	Foliar spraying or atomizing spraying	0.048 - 0.19	400 – 1600[2]	0.012[2]	2-4	28

[1]Application rate for a standard tree of 3 m height (0.06 kg ai/ha, 500 l water/ha per m tree height)
[2] Standard application = 1600 l water/ha, 0.012 kg ai/ha. Higher concentration for low volume (atomizing) spraying

RESIDUES RESULTING FROM SUPERVISED TRIALS

Pome fruit. The 1996 JMPR evaluated eight German trials on apples according to Belgium GAP (3 x 0.12 kg ai/ha, 0.012 kg ai/hl, PHI 28 days) as the more severe German GAP was pending. The data are re-evaluated against German GAP in Table 2.

Table 2. Residues of tebufenozide from supervised trials on apples in Germany (1996 JMPR).

Reference, location, year	Form.	Application rate per treatment		No. of of treatments	PHI, days	Residues, mg/kg
		kg ai/ha	kg ai/hl			
Raquet *et al*, 1993, Drage-Elbersdorf, 1992	SC	0.19	0.013	3	0 7 14 28	0.29 0.24 0.24 0.16
Raquet *et al*, 1993, Bornheim, 1992	SC	0.16	0.013	3	0 7 14 28	0.05 0.03 0.02 <0.02

Reference, location, year	Form.	Application rate per treatment		No. of of treatments	PHI, days	Residues, mg/kg
		kg ai/ha	kg ai/hl			
Raquet *et al*, 1993, Bodenegg, 1992	SC	0.2	0.013	3	0 7 14 28	0.39 0.28 0.35 0.2
Raquet *et al*, 1993, Hoechst, 1992	SC	0.12	0.013	3	0 7 14 28	0.27 0.2 0.11 0.08
Raquet *et al*, 1993, Niederdorfelden, 1992	SC	0.12 0.13	0.013	1 2	0 7 14 21	0.13 0.15 0.06 0.11
Brusche and Holzwarth, 1995, Drage-Elbersdorf, 1993	SC	0.18	0.012	3	12 25	0.15 0.16
Brusche and Holzwarth, 1995, Drage-Elbersdorf, 1993	SC	0.18	0.012	3	13 27	0.15 0.09
Brusche and Holzwarth, 1995, Kippenhausen, 1993	SC	0.18	0.012	3	12 27	0.21 0.23

Grapes. Nine German trials were reported to the 1996 JMPR but could not be evaluated because German GAP was pending. The data are evaluated against German GAP in Table 3.

Table 3. Residues of tebufenozide from supervised trials on grapes in Germany (JMPR 1996).

Reference, year	Form.	Application rate per treatment			No. of treatments	PHI, days	Residues, mg/kg
		kg ai/ha	Water, l/ha	kg ai/hl			
Ulrich *et al.*, 1994	SC	0.077 0.077 0.2 0.2	615 615 541 529 *(1600)*[1]	0.013 0.013 0.037 0.038 *(0.013)*[1]	1 1 1 1	0 7 14 28	0.59 0.48 1.1 0.28
Ulrich *et al.*, 1994	SC	0.074 0.079 0.185 0.2	580 612 483 516 *(1600)*[1]	0.013 0.013 0.038 0.038 *(0.012)*[1]	1 1 1 1	0 7 14 28	0.37 0.2 0.44 0.5
Ulrich *et al.*, 1994	SC	0.074 0.077 0.19 0.21	585 602 499 550 *(1600)*[1]	0.013 0.013 0.038 0.038 *(0.013)*[1]	1 1 1 1	0 7 14 28	0.5 0.28 0.79 0.24
Ulrich *et al.*, 1994	SC	0.074 0.077 0.2 0.2	591 606 535 525 *(1600)*[1]	0.013 0.013 0.038 0.038 *(0.012)*[1]	1 1 1 1	0 7 14 28	0.33 0.53 0.47 0.27
Ulrich *et al.*, 1994	SC	0.074 0.077 0.21 0.2	587 599 542 519 *(1600)*[1]	0.013 0.013 0.038 0.038 *(0.012)*[1]	1 1 1 1	0 7 14 28	0.54 0.57 0.4 0.4

Reference, year	Form.	Application rate per treatment			No. of treatments	PHI, days	Residues, mg/kg
		kg ai/ha	Water, l/ha	kg ai/hl			
Kaiser, 1994	SC	0.073	575	0.013	1	0	0.52
		0.079	625	0.013	1	7	0.95
		0.19	500	0.038	1	14	0.16
		0.21	550	0.038	1	28	0.21
			(1600)[1]	*(0.013)*[1]			
Kaiser, 1994	SC	0.079	625	0.013	1	0	0.33
		0.073	604	0.012	1	7	0.5
		0.2	541	0.037	1	14	0.15
		0.2	541	0.037	1	28	0.26
			(1600)[1]	*(0.125)*[1]			
Kaiser, 1994	SC	0.075	586	0.013	1	0	0.46
		0.074	579	0.013	1	7	0.42
		0.2	531	0.038	1	14	0.64
		0.2	510	0.038	1	28	0.22
			(1600)[1]	*(0.012)*[1]			
Kaiser, 1994	SC	0.079	621	0.013	1	0	0.46
		0.076	596	0.013	1	7	0.32
		0.21	540	0.038	1	14	0.28
		0.2	527	0.038	1	28	0.42
			(1600)[1]	*(0.0125)*[1]			

[1] Concentration (kg ai/hl) of last treatment calculated according to the standard water volume of 1600 l/ha

APPRAISAL

The insecticide tebufenozide was first evaluated by the 1996 JMPR when an ADI was allocated and MRLs for pome fruits, grapes, walnut and husked rice were recommended. German data on supervised residue trials on apples and grapes were provided to the 1996 Meeting, but could not be evaluated against German GAP because it was only pending. The present Meeting received information on currently registered GAP in Germany for re-evaluation of tebufenozide residues in grapes and pome fruit.

Pome fruit. The residues in the German trials on apples evaluated according to the new German GAP were 0.02, 0.11, 0.11, 0.15, 0.16, 0.23, 0.24 and 0.35 mg/kg. The German GAP has a PHI of 14 days and would be expected to produce higher residues than the Belgian GAP (PHI 28 days) which was used by the 1996 JMPR for the evaluation of the German trials (giving residues of <0.02, 0.08, 0.09, 0.11, 0.16, 0.16, 0.2 and 0.23 mg/kg). The Meeting agreed to replace the 28-day residues of the 1996 evaluation by the corresponding residues at 14 days, giving residues in pome fruit in rank order of 0.01, 0.02, 0.02, 0.05, 0.07, 0.077, 0.08, 0.09, 0.1, 0.1, 0.11, 0.11, 0.11, 0.12, 0.14, 0.14, 0.15, 0.16, 0.16, 0.18, 0.19, 0.23, 0.23, 0.24, 0.26, 0.27, 0.28, 0.32, 0.35, 0.37, 0.37, 0.43, 0.52, 0.52, 0.55, 0.75, 0.84 and 1.1 mg/kg.

The Meeting agreed to recommend retention of the current CXL of 1 mg/kg for pome fruits and estimated an STMR of 0.17 mg/kg (previous STMR 0.16 mg/kg).

Processing factors of 2.5, 0.25 and 0.125 for apple pomace (wet), purée and juice respectively were reported by the 1996 JMPR. On the basis of the new STMR for pome fruits the Meeting estimated STMRs of 0.425 mg/kg for wet apple pomace, 0.0425 mg/kg for apple purée and 0.021 mg/kg for apple juice.

Grapes. The German residue data from 1996 evaluated according to current German GAP in rank order were 0.21, 0.22, 0.24, 0.26, 0.27, 0.28, 0.4, 0.42 and 0.5 mg/kg.

The nine trials in France in 1996 complied with GAP (3 applications at 0.144 kg ai/ha, 21 days PHI) and showed the residues 0.05, 0.06, 0.07, 0.08, 0.12, 0.18, 0.26, 0.28 and 0.28 mg/kg.

The rank order of the combined German and French trials was 0.05, 0.06, 0.07, 0.08, 0.12, 0.18, 0.21, 0.22, 0.24, 0.26, 0.26, 0.27, 0.28, 0.28, 0.28, 0.4, 0.42 and 0.5 mg/kg.

On the basis of the German and French trials, the Meeting estimated a maximum residue level of 1 mg/kg for grapes to replace current draft MRL (0.5 mg/kg) and an STMR of 0.25 mg/kg.

Processing factors of 0.25 and 2.7 for wine and grape pomace (wet) respectively, were reported by the 1996 JMPR. The Meeting estimated STMRs of 0.0625 mg/kg for wine and 0.675 mg/kg for wet grape pomace from the STMR of 0.25 mg/kg for grapes.

RECOMMENDATIONS

The Meeting estimated the following maximum residue levels which are recommended for use as MRLs.

Definition of residue for compliance with MRLs and for the estimation of dietary intake: tebufenozide.

The compound is fat-soluble.

Commodity		MRL, mg/kg		STMR, mg/kg
CCN	Name	New	Previous	
FP 0009	Pome fruits	1	1	0.17
	Apple pomace, wet			0.43
JF 0226	Apple juice			0.021
	Apple purée			0.043
FB 0269	Grapes	1	0.5	0.25
	Grape pomace, wet			0.68
	Wine			0.063

DIETARY RISK ASSESSMENT

Chronic intake

STMRs were estimated for 4 commodities (1999: pome fruits, grapes; 1996: walnuts, rice).

International Estimated Daily Intakes for the 5 GEMS/Food regional diets, based on estimated STMRs, were in the range of 0–1% of the ADI. The Meeting concluded that intake of residues of tebufenozide resulting from its uses that have been considered by the JMPR is unlikely to present a public health concern.

Acute intake

The international estimate of short-term intake (IESTI) for tebufenozide was calculated for the commodities for which MRLs and STMRs were established and for which consumption data (large portion consumption and unit weight) were available. The results are shown in Annex IV. The IESTI varied from 0.001 to 0.015 mg/kg bw for the general population and from 0 to 0.058 mg/kg bw for children. As no acute reference dose has been established, the acute risk assessment for tebufenozide was not finalized.

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ANNEX I

ADIs, ACUTE REFERENCE DOSES, RECOMMENDED MRLs AND STMRs RECORDED BY THE 1999 MEETING

The Table includes maximum Acceptable Daily Intakes (ADIs), Acute Reference Doses (acute RfDs), recommendations for Maximum Residue Limits (MRLs), and Supervised Trials Median Residue (STMR) levels. Compounds whose estimated dietary intakes might, on the basis of the available information, exceed their ADIs are marked with footnotes. A proposal to distinguish such compounds from those whose intakes are clearly below the corresponding ADIs was made at the 1997 Joint Meeting and its rationale is described in detail in the 1997 report (Section 2.3). It should be noted that this distinction applies only to new compounds and those re-evaluated within the CCPR Periodic Review Programme.

STMR levels were introduced in 1996 in response to recommendations of a Joint FAO/WHO Consultation on Guidelines for Predicting the Dietary Intake of Pesticide Residues held in York, UK, in 1995. The 1996 JMPR report explains the reasons for their introduction and gives details of the procedures used in their calculation (Sections 2.2.1, 2.2.3, Annex IV and the introduction to Annex I).

In general, the MRLs recommended for compounds which have been reviewed previously are additional to, or amend, those recorded in the reports of earlier Meetings. If a recommended MRL is an amendment the previous value is also recorded. All recommendations for compounds re-evaluated in the CCPR Periodic Review Programme are listed however (even if identical to existing CXLs or draft MRLs) because such re-evaluations replace the original evaluation rather than supplement it.

Some ADIs may be temporary: this is indicated by the letter T and the year in which re-evaluation is scheduled in parenthesis below the ADI. All recommended MRLs for compounds with temporary ADIs are necessarily temporary, but some recommendations are designated as temporary (TMRLs) until required information has been provided and evaluated, irrespective of the status of the ADI. Such recommendations are followed by the letter T in the table. (See also the list of qualifications and abbreviations below.)

The Table includes the Codex reference numbers of the compounds and the Codex Classification Numbers (CCNs) of the commodities, to facilitate reference to the Codex Maximum Limits for Pesticide Residues (*Codex Alimentarius,* Vol. 2B) and other documents and working documents of the Codex Alimentarius Commission. Commodities are listed in alphabetical order.

Apart from the abbreviations indicated above, the following qualifications are used in the Table.

* following recommended MRL	At or about the limit of determination
* following name of pesticide	New compound
** following name of pesticide	Compound reviewed in CCPR Periodic Review Programme

Po	The recommendation accommodates post-harvest treatment of the commodity.
T	Temporary
W in place of a recommended MRL	The previous recommendation is withdrawn, or withdrawal of the recommended MRL or existing Codex or draft MRL is recommended

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
Bentazone (172)	0.1	Acute RfD: unnecessary				
Bitertanol **	0.01	JF 0226	Apple juice			0.034
(144)		AB 0226	Apple pomace, dry			1.78
			Apple pomace, wet			0.648
			Apple sauce			0.035
		FS 0240	Apricot	W	1	
		FI 0327	Banana	0.5	0.5	0.075
		GC 0640	Barley	0.05 *		0
		AS 0640	Barley straw and fodder, dry	0.05 *		0
		AL 1030	Bean forage (green)	W	10	
		FS 0013	Cherries	1	2	0.365
			Cherry jam			0.16
			Cherry juice			0.062
			Cherry preserve			0.22
		VP 0526	Common bean (pods and/or immature seeds)	W	0.5	
		VC0424	Cucumber	0.5	0.5	0.18
		MO 0105	Edible offal (Mammalian)	0.05*		0.05
		PE 0112	Eggs	0.01 *		0
		MM 0095	Meat (from mammals other than marine mammals)	0.05* (fat)		0.05
		ML 0106	Milks	0.05*		0.05
		FS 0245	Nectarine	1	1	0.20
		AF 0647	Oat forage (green)	0.05 *[1]	0.1 *	0.05
		AS 0647	Oat straw and fodder, dry	0.05 *	0.1 *	0
		GC 0647	Oats	0.05 *	0.1 *	0
		FS 0247	Peach	1	1	0.20
		SO 0697	Peanut	W	0.1 *	
		AL 1270	Peanut forage (green)	W	20	
		FS 0014	Plums (including Prunes)	2	2	0.34
			Plum jam			0.21
		FP 0009	Pome fruits	2	2	0.24

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		PM 0110	Poultry meat	0.01 *		0
		PO 0111	Poultry, Edible offal of	0.01 *		0
		GC 0650	Rye	0.05 *	0.1 *	0
		AF 0650	Rye forage (green)	0.05 *[1]	0.1 *	0.05
		AS 0650	Rye straw and fodder, dry	0.05 *	0.1 *	0
		VO 0448	Tomato	3		0.76
		JF 0448	Tomato juice			0.1
			Tomato paste			1.6
			Tomato preserve			0.28
		GC 0653	Triticale	0.05 *		0
			Triticale straw and fodder, dry	0.05 *		0
		GC 0654	Wheat	0.05 *	0.1 *	0
		AS 0654	Wheat straw and fodder, dry	0.05 *	0.1 *	0
		Residue for compliance with MRLs for plant and animal commodities: bitertanol For estimation of dietary intake for plant commodities: bitertanol For estimation of dietary intake for animal commodities: sum of bitertanol, *p*-hydroxybitertanol and acid-hydrolysable conjugates of *p*-hydrroxybiternol The residue is fat-soluble Acute RfD: unnecessary [1]Dry weight Periodic review was for residues only				
Buprofezin (173)	0.01	FC 0004	Oranges, Sweet, Sour	0.5	0.3 T[1]	0.011
		JF 0004	Orange juice			0.012
			Orange pulp, dry			0.27
		Residue (for MRLs and STMRs): buprofezin The residue is fat-soluble Acute RfD: unnecessary [1]Withdrawal recommended by 1995 JMPR				
Carbofuran (096)	0.002	FC 0206	Mandarin	0.5		0.1
		Residue (for MRLs and STMRs): sum of carbofuran and 3-hydroxycarbofuran, expressed as carbofuran. Acute RfD: may be necessary but has not yet been established.				
Carbosulfan (145)	0.01	FC 0206	Mandarin	0.1		0.01
		Residue (for MRLs and STMRs): carbosulfan Acute RfD: may be necessary but has not yet been established.				
Chlormequat (015)	0.05	Acute RfD: 0.05 mg/kg bw				
Chlorpyrifos ** (017)	0.01	Acute RfD: 0.1 mg/kg bw ADI unchanged Periodic review was for toxicology only				
Clethodim (187)	0.01	VD 0071	Beans (dry)	2	0.1[1]	0.81
		AL 0061	Bean fodder (hay)	10		1.8
		AL 1030	Bean forage (green)	5		1.5
		MO 1280	Cattle, kidney	W	0.2*	
		MO 1281	Cattle, liver	W	0.2*	
		MM 0812	Cattle meat	W	0.5*	
		ML 0812	Cattle milk	W	0.1*	

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		PE 0840	Chicken eggs	W	0.5*	
		PM 0840	Chicken meat	W	0.5*	
		MO 0105	Edible offal (Mammalian)	0.2*		0
		PE 0112	Eggs	0.05*		0
		MM 0095	Meat (from mammals other than marine mammals)	0.2*		0
		ML 0106	Milks	0.05*		0
		OC 0697	Peanut oil, crude			0.52
		OR 0697	Peanut oil, edible			0.12
		VR 0589	Potato[2]	0.5	0.2	
		PO 0111	Poultry, Edible offal of	0.2*		0
		PM 0110	Poultry meat	0.2*		0
		SO 0702	Sunflower seed	0.5	0.2 [1]	0.06
		OC 0702	Sunflower seed oil, crude	0.1*	0.05 [1]	0.012
		JF 0448	Tomato juice			0.27
			Tomato paste			1.2
			Tomato purée			0.77
		Residue (for MRLs and STMRs): sum of clethodim and metabolites containing 5-(2-ethylthiopropyl)cyclohexene-3-one and 5-(2-ethylthiopropyl)-5-hydroxycyclohexene-3-one moieties and their sulfoxides and sulfones, expressed as clethodim Acute RfD: unnecessary [1]Withdrawal was recommended by 1997 JMPR [2]STMR could not be estimated as the previously reviewed data from France, Italy and Ukraine were not re-submitted				
Diazinon (022) [1]	0.002	JF 0226	Apple juice			0.0004
			Apple pomace, wet			0.057
			Apple sauce			0.0004
			Apple slices, canned			0.0004
		VB 0041	Cabbages, Head	0.5	2	0.01
		MM 0814	Goat meat	2 (fat) V	2 (fat) V	0.3 (fat) [2] 0.02 (whole muscle) [2]
		MO 0098	Kidney of cattle, goats, pigs and sheep	0.03 V	0.03 V	0.01[2]
		MO 0099	Liver of cattle, goats, pigs and sheep	0.03 V	0.03 V	0.01[2]
		MM 0097	Meat of cattle, pigs and sheep	2 (fat) V	2 (fat) V	0.3 (fat) [2] 0.02 (whole muscle) [2]
		ML 0106	Milks	0.02 F V	0.02 F V	0.02[2]
		FP 0009	Pome fruits	0.3	2	0.04
		Residue (for MRLs and STMRs): diazinon The residue is fat-soluble Acute RfD: may be necessary but has not yet been established [1] Estimated dietary intake might, on the basis of the available information, exceed the ADI. [2] STMR estimated by the 1996 JMPR.				
Dimethipin ** (151)	0.02	Acute RfD: 0.02 mg/kg bw ADI unchanged Periodic review was for toxicology only.				
Dinocap (087)	0.008	VO 0448	Tomato	0.3		0.045

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		Residue (for MRLs and STMRs): sum of dinocap isomers and dinocap phenols, expressed as dinocap Acute RfD: 0.008 mg/kg bw				
Ethephon (106)	0.05	VC 4199	Cantaloupe	1	1	0.24 [1]
		DF 0269	Dried grapes (Currants, Raisins and Sultanas)	5		0.84
		FB 0269	Grapes	1	1	0.31
		VO 0051	Peppers	5	30	0.98
		FI 0353	Pineapple	2	1	0.13
			Pineapple, canned			0.036
		JF 0341	Pineapple juice			0.051
		VO 0448	Tomato	2	2	0.41
		JF 0448	Tomato juice			0.14
			Tomato paste			0.31
			Wine			0.31
		Residue (for MRLs and STMRs): ethephon [1] STMR expressed on whole fruit, not edible portion Acute RfD: may be necessary but has not yet been established.				
Ethoprophos ** (149)	0.0004	Acute RfD: 0.05 mg/kg bw Previous ADI: 0.0003 mg/kg bw Periodic review was for toxicology only.				
Ethoxyquin ** (035)	0.005	FP 0230	Pear	W	3 Po	
		Residue for compliance with MRLs: ethoxyquin. The residue for the estimation of dietary intake cannot be defined until the toxicities of the plant metabolites are known Acute RfD: unnecessary Periodic review was for residues only.				
Fenamiphos ** (085)	0.0008	FP 0226	Apple	0.05*		0.01
		JF 0226	Apple juice			0.0078
		FI 0327	Banana[1]	0.05*	0.1	0.02
		VB 0400	Broccoli	W	0.05*	
		VB 0402	Brussels sprouts	0.05	0.05*	0.01
		VB 0041	Cabbages, Head[1,2]	0.05	0.05*	0.01
		VR 0577	Carrot[1,2]	0.2	0.2	0.02
		VB 0404	Cauliflower	W	0.05*	
		SB 0716	Coffee beans	W	0.1	
		SM 0716	Coffee beans, roasted	W	0.1	
		SO 0691	Cotton seed	0.05*	0.05*	0
		OC 0691	Cotton seed oil, crude	0.05*		0.01
		MO 0105	Edible offal (Mammalian)	0.01*		0
		PE 0112	Eggs	0.01*		0
		FB 0269	Grapes[1,2]	0.1	0.1	0.02

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		JF 0269	Grape juice			0.009
		FI 0341	Kiwifruit	W	0.05*	
		MM 0095	Meat (Mammalian)	0.01*		0
		VC 0046	Melons, except Watermelon[1,2]	0.05*	0.05*	0.02
		ML 0106	Milks	0.005*		0
		FC 0004	Oranges, Sweet, Sour	W	0.5	
		SO 0697	Peanut	0.05*	0.05*	0
		OC 0697	Peanut oil, crude	0.05*		0
		VO 0051	Peppers[1,2]	0.5		0.055
		FI 0353	Pineapple[1,2]	0.05*	0.05*	0.01
			Pineapple juice, canned			0.012
			Pineapple juice, raw			0.006
		VR 0589	Potato	W	0.2	
		PO 0111	Poultry, Edible offal of	0.01*		0
		PM 0110	Poultry meat	0.01*		0
		VD 0541	Soya bean (dry)	W	0.05*	
		VR 0596	Sugar beet	W	0.05*	
		VR 0508	Sweet potato	W	0.1	
		VO 0448	Tomato[1,2]	0.5	0.2	0.05
		JF 0448	Tomato juice			0.05
		VC 0432	Watermelon[1,2]	0.05*		0.02
		Residue (for MRLs and STMRs): sum of fenamiphos, its sulfoxide and sulfone, expressed as fenamiphos Acute RfD: 0.0008 mg/kg bw (1997) Periodic review was for residues only [1]The information provided to the JMPR precludes an estimate that the acute dietary intake for children would be below the acute reference dose [2]The information provided to the JMPR precludes an estimate that the acute dietary intake for the general population would be below the acute reference dose				
Fenpropimorph (188)	0.003	FI 0327	Banana	2		0.11
		PE 0112	Eggs	0.01*		0
		MO 0098	Kidney of cattle, goats, pigs and sheep	0.05		0.026
		MO 0099	Liver of cattle, goats, pigs and sheep	0.3		0.22
		MF 0100	Mammalian fats (except milk fats)	0.01		0.006
		MM 0095	Meat (from mammals other than marine mammals)	0.02		0.009
		ML 0106	Milks	0.01		0.004
		PF 0111	Poultry fats	0.01*		0
		PM 0111	Poultry meat	0.01*		0
		PO 0111	Poultry, Edible offal of	0.01*		0
		Residue for compliance with MRLs and estimation of dietary intake for plant commodities: fenpropimorph For compliance with MRLs and estimation of dietary intake for animal commodities: 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid expressed as fenpropimorph. Acute RfD: may be necessary but has not yet been established.				
Fenpyroximate (193)	0.01	FP 0226	Apple	0.3		0.09

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		JF 0226	Apple juice			0.04
			Apple purée			0.05
			Beer			0.004
		MO 1280	Cattle, kidney	0.01*		0
		MO 1281	Cattle, liver	0.01*		0
		MM 0812	Cattle meat	0.02 (fat)		0.01
		ML 0812	Cattle milk	0.005* F		0.002
		FB 0269	Grapes	1		0.07
		DH 1100	Hops	10		4.4
		FC 0004	Oranges, Sweet, Sour	0.2		0.01
			Wine			0.005
		Residue (for MRLs and STMRs): fenpyroximate The residue is fat-soluble. Acute RfD: may be necessary but has not yet been established.				
Folpet (041)	0.1	FP 0226	Apple	10	10 [1]	3.1
		JF 0226	Apple juice			0.11
			Apple pomace, wet			8.1
		VC 0424	Cucumber	1	0.5 [2]	0.36
		DF 0269	Dried grapes (Currants, Raisins and Sultanas)	40	40 [1]	8.0
		FB 0269	Grapes	10	10 [1]	2.5
		JF 0269	Grape juice			0.0075
		VL 0482	Lettuce, Head	50		14
		VC 0046	Melons, except Watermelon	3	3 [2]	0.41
		VA 0385	Onion, Bulb	1		0.07
		VR 0589	Potato	0.1	0.02*[2]	0.01
		FB 0275	Strawberry	5	5 [1]	1.6
		VO 0448	Tomato	3	3 [1]	0.90
			Tomato paste			0.025
			Tomato purée			0.025
			Wine			0
		Residue (for MRLs and STMRs): folpet [1]The 1998 JMPR recommended withdrawal of current MRLs because critical supporting studies on the environmental fate of folpet were not provided. [2]Recommended for withdrawal by 1998 JMPR Acute RfD: may be necessary but has not yet been established				
Glufosinate-ammonium (175)	0.02[1]	MO 0105	Edible offal (Mammalian)	0.1*		0
		PE 0112	Eggs	0.05*		0.05 [2]
		AS 0645	Maize fodder	10		0.72
		AF 0645	Maize forage	5	0.2	0.54
		MM 0095	Meat (from mammals other than marine mammals)	0.05*		0
		ML 0106	Milks	0.02*		0
		PM 0110	Poultry meat	0.05*		0.05 [2]
		PO 0111	Poultry, Edible offal of	0.1*		0.1 [2]
		VD 0541	Soya bean (dry)	2	0.1	0.87

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		Residue (for MRLs and STMRs): sum of glufosinate-ammonium, 3-[hydroxy(methyl)phosphinoyl]propionic acid and *N*-acetyl-glufosinate, expressed as glufosinate (free acid). [1]Group ADI for glufosinate-ammonium, 3-[hydroxy(methyl)phosphinoyl]propionic acid and *N*-acetyl-glufosinate, alone or in combination. [2]LOD is assigned as STMR level Previous ADI: 0.02 mg/kg bw (1991) Acute RfD: unnecessary				
Malathion ** (049)	0.3	AL 1020	Alfalfa fodder	200		17
		AL 1021	Alfalfa forage (green)	500 (dry weight)		157 (dry weight)
		FP 0226	Apple	W	2	
		VS 0621	Asparagus	1		0.305
		VP 0071	Beans (dry)	2	8 Po	0.36
		VP 0061	Beans, except Broad bean and Soya bean	1		0.31
		FB 0264	Blackberries	W	8	
		FB 0020	Blueberries	10	0.5	2.27
		VB 0400	Broccoli	W	5	
		VB 0041	Cabbages, Head	W	8	
		VB 0404	Cauliflower	W	0.5	
		VS 0624	Celery	W	1	
		GC 0080	Cereal grains	W	8 Po	
		VL 0464	Chard	W	0.5	
		FS 0013	Cherries	W	6	
		FC 0001	Citrus fruits	W	4	
		AL 1023	Clover	500 (dry weight)		168 (dry weight)
		AL 1031	Clover hay or fodder	150		33.5
		VP 0526	Common bean (pods and/or immature seeds)	W	2	
		SO 0691	Cotton seed	20		4.8
			Cotton seed meal			0.34
			Cotton seed oil, blanched and deodorized			0.038
		OC 0691	Cotton seed oil, crude	13		3.21
		OR 0691	Cotton seed oil, edible	13		3.12
		VC 0424	Cucumber	0.2		0.02
		DF 0167	Dried fruits	W	8	
		VO 0440	Egg plant	W	0.5	
		VL 0476	Endive	W	8	
		FB 0269	Grapes	W	8	
		AF 0162	Grass forage	200	-	49.5
		AS 0162	Hay or fodder (dry) of grasses	300	-	44
		VL 0480	Kale	W	3	
		VB 0405	Kohlrabi	W	0.5	
		VD 0533	Lentil (dry)	W	8	
		VL 0482	Lettuce, Head	W	8	
		GC0645	Maize	0.05		0.01
		AS 0645	Maize fodder	50		6.65
		AF 0645	Maize forage	10 (dry weight)		0.20 (dry weight)
		VL 0485	Mustard greens	2		0.07
			Nuts (whole in shell)	W	8	
		VA 0385	Onion, Bulb	1		0.23
		FS 0247	Peach	W	6	
		FP 0230	Pear	W	0.5	

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		VP 0063	Peas (pods and succulent = immature seeds)	W	0.5	
		VO 0051	Peppers	0.1	0.5	0.01
		FS 0014	Plums (including Prunes)	W	6	
		FB 0272	Raspberries, Red, Black	W	8	
		VR 0075	Root and tuber vegetables [1]	W	0.5	
		CM 0650	Rye bran, unprocessed	W	20 PoP	
		CF 1250	Rye flour	W	2 PoP	
		CF 1251	Rye wholemeal	W	2 PoP	
		GC 0651	Sorghum	3		0.235
		VL 0502	Spinach	3	8	0.35
		VA 0389	Spring onion	5		0.52
		FB 0275	Strawberry	1	1	0.25
		VO 0447	Sweet corn (corn-on the-cob)	0.02		0.01
		VO 0448	Tomato	0.5	3	0.21
		JF 0448	Tomato juice	0.01		0
			Tomato ketchup			0.09
			Tomato pomace, wet			0.20
			Tomato pomace, dry			1.6
			Tomato purée			0.07
		VR 0506	Turnip, Garden	0.2	3	0.05
		VL 0506	Turnip greens	5		1.20
		GC 0654	Wheat	0.5		0.04
			Wheat forage	20 (dry weight)		4.14 (dry weight)
		AS 0654	Wheat straw and fodder, dry	50		6.85
		Residue (for MRLs and STMRs): malathion [1] Except Turnip, Garden Periodic review was for residues only. Acute RfD: may be necessary but has not yet been established.				
Methiocarb** (132)	0.02	VS 0620	Artichoke, Globe	W	0.05 *	
		VB0400	Broccoli	W	0.2	
		VB0402	Brussels sprouts	W	0.2	
		VB0041	Cabbages, Head	W	0.2	
		VB0404	Cauliflower	W	0.2	
		GC0080	Cereal grains	W	0.05 *	
		FC 0001	Citrus fruits	W	0.05 *	
		PE 0840	Eggs	W	0.05 *	
		TN 0666	Hazelnuts	W	0.05 *	
		VL 0482	Lettuce, Head	W	0.2	
		VL 0483	Lettuce, Leaf	W	0.2	
		MM0095	Meat (from mammals other than marine mammals)	W	0.05 *	
		ML0106	Milks	W	0.05 *	
		PM 0110	Poultry meat	W	0.05 *	

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		SO 0495	Rape seed	W	0.05 *	
		FB 0275	Strawberry	1		0.44
		VR 0596	Sugar beet	W	0.05 *	
		VO 0447	Sweet corn (corn-on-the-cob)	W	0.05 *	
		Residue (for MRLs and STMRs): sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb. Acute RfD: 0.02 mg/kg bw Periodic review was for residues only.				
Oxydemeton-methyl (166)	0.0003	ADI is for demeton-S-methyl and related compounds, alone or in combination Acute RfD: may be necessary but has not yet been established.				
Permethrin ** (120)	0.05[1]	Acute RfD: unnecessary [1]For technical-grade permethrin with *cis*-: *trans*- ratios of 25:75 to 40:60. ADI unchanged Periodic review was for toxicology only.				
2-Phenylphenol ** (056)	0.4	FP 0226	Apple	W	25 Po	
		FC 0001	Citrus fruits	10	10 Po	0.20
		AB 0001	Citrus pulp, dried	60		
		JF 0004	Orange juice	0.5		0.12
			Orange oil			340
		FP 0230	Pear	W	25 Po	
		Residue (for MRLs and STMRs): Plant commodities: sum of 2-phenylphenol and sodium 2-phenylphenate, free and conjugated, expressed as 2-phenylphenol Previous ADI: 0.02 mg/kg bw (1990) Acute RfD: unnecessary				
Phosalone (060)	0.02	TN 0660	Almonds	0.1	-	0.05
			Apple compote		-	0.1
		TN 0666	Hazelnuts	0.05*	-	0.05
		FP 0009	Pome fruits	2	-[1]	0.8
		FS 0012	Stone fruits	2	-	0.45
		TN 0678	Walnuts	0.05*	-	0.05
		Residue (for MRLs and STMRs): phosalone The residue is fat-soluble. Acute RfD: may be necessary but has not yet been established [1]A CXL of 5 mg/kg for apple was recommended for withdrawal by the 1994 JMPR				
Propargite **[1] (113)	0.01	Acute RfD: unnecessary Previous ADI: 0.15 mg/kg bw Periodic review was for toxicology only. [1]The information provided to the JMPR precludes an estimate that the dietary intake would be below the ADI.				
Propylenethiourea	0.0003	Acute RfD: 0.003 mg/kg bw Previous temporary ADI: 0.0002 mg/kg bw				
Pyrethrins ** (063)	0.04	Acute RfD: 0.2 mg/kg bw ADI unchanged Periodic review was for toxicology only.				
Pyriproxifen * (200)	0.1	MM0812	Cattle meat	0.01* (fat)		0
		MO0812	Cattle, Edible offal of	0.01*		0
		FC 0001	Citrus fruits	1		0.013

Pesticide	ADI, mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
			Cotton gin trash	5		0.91
		SO 0691	Cotton seed	0.05		0.01
			Cotton seed meal			0.001
		OC 0691	Cotton seed oil, crude	0.01		0.002
		OR 0691	Cotton seed oil, edible	0.01		0.002
		MM0814	Goat meat	0.01* (fat)		0
		MO 0814	Goat, Edible offal of	0.01*		0
		Residue (for MRLs and STMRs): pyriproxifen The residue is fat-soluble. Acute RfD: unnecessary New compound				
Tebufenozide (196)	0.02	JF 0226	Apple juice			0.021
			Apple pomace, wet			0.425
			Apple purée			0.043
		FB 0269	Grapes	1	0.5	0.25
			Grape pomace, wet			0.675
		FP 0009	Pome fruits	1	1	0.17
			Wine			0.063
		Residue (for MRLs and STMRs): tebufenozide The residue is fat-soluble. Acute RfD: may be necessary but has not yet been established.				

ANNEX II

PREVIOUS FAO AND WHO DOCUMENTS

1. FAO/WHO. 1962 Principles governing consumer safety in relation to pesticide residues. Report of a meeting of a WHO Expert Committee on Pesticide Residues held jointly with the FAO Panel of Experts on the Use of Pesticides in Agriculture. FAO Plant Production and Protection Division Report, No. PL/1961/11; WHO Technical Report Series, No. 240.

2. FAO/WHO. 1964 Evaluations of the toxicity of pesticide residues in food. Report of a Joint Meeting of the FAO Committee on Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues. FAO Meeting Report, No. PL/1963/13; WHO/Food Add./23.

3. FAO/WHO. 1965a Evaluations of the toxicity of pesticide residues in food. Report of the Second Joint Meeting of the FAO Committee on Pesticides in Agriculture and the WHO Expert Committee on Pesticide Residues. FAO Meeting Report, No. PL/1965/10; WHO/Food Add./26.65.

4. FAO/WHO. 1965b Evaluations of the toxicity of pesticide residues in food. FAO Meeting Report, No. PL/1965/10/1; WHO/Food Add./27.65.

5. FAO/WHO. 1965c Evaluation of the hazards to consumers resulting from the use of fumigants in the protection of food. FAO Meeting Report, No. PL/1965/10/2; WHO/Food Add./28.65.

6. FAO/WHO. 1967a Pesticide residues in food. Joint report of the FAO Working Party on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Agricultural Studies, No. 73; WHO Technical Report Series, No. 370.

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11. FAO/WHO. 1969b 1968 Evaluation of some pesticide residues in food. FAO/PL:1968/M/9/1; WHO/Food Add./69.35.

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1970a of the FAO Working Party of experts on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Agricultural Studies, No. 84; WHO Technical Report Series, No. 458.

13. FAO/WHO. 1969 Evaluation of some pesticide residues in food.
1970b FAO/PL:1969/M/17/1; WHO/Food Add./70.38

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1971a of the FAO Working Party of experts on Pesticide Residues and the WHO Expert Committee on Pesticide Residues. FAO Agricultural Studies, No. 87; WHO Technical Report Series, No. 474.

15. FAO/WHO. 1970 Evaluation of some pesticide residues in food.
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16. FAO/WHO. Pesticide residues in food. Report of the 1971 Joint Meeting
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17. FAO/WHO. 1971 Evaluation of some pesticide residues in food.
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18. FAO/WHO. Pesticide residues in food. Report of the 1972 Joint Meeting
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25. FAO/WHO. 1975 Evaluation of some pesticide residues in food.
1976b AGP:1975/M/13; WHO Pesticide Residues Series, No. 5.

26. FAO/WHO. 1977a Pesticide residues in food. Report of the 1976 Joint Meeting of the FAO Panel of Experts on Pesticide Residues and the Environment and the WHO Expert Group on Pesticide Residues. FAO Food and Nutrition Series, No. 9; FAO Plant Production and Protection Series, No. 8; WHO Technical Report Series, No. 612.

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30. FAO/WHO. 1979a Pesticide residues in food - 1978. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues and the Environment and the WHO Expert Group on Pesticide Residues. FAO Plant Production and Protection Paper 15.

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33. FAO/WHO. 1980b Pesticide residues in food: 1979 evaluations. FAO Plant Production and Protection Paper 20 Sup.

34. FAO/WHO. 1981a Pesticide residues in food - 1980. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Expert Group on Pesticide Residues. FAO Plant Production and Protection Paper 26.

35. FAO/WHO. 1981b Pesticide residues in food: 1980 evaluations. FAO Plant Production and Protection Paper 26 Sup.

36. FAO/WHO. 1982a Pesticide residues in food - 1981. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Expert Group on Pesticide Residues. FAO Plant Production and Protection Paper 37.

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38. FAO/WHO. 1983a Pesticide residues in food - 1982. Report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Expert Group on Pesticide Residues. FAO Plant Production and Protection Paper 46.

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