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Pesticide residues in food 1995

Joint FAO/WHO Meeting on Pesticide Residues

EVALUATIONS

1995

PART I - RESIDUES

Rome, 1996

CONTENTS

[1] * First evaluation
** Evaluation in CCPR periodic review programme

ABBREVIATIONS WHICH MAY BE USED

Ache	acetylcholinesterase
ADI	acceptable daily intake
AFI(D)	alkali flame-ionization (detector)
ai	active ingredient
ALAT	alanine aminotransferase
approx.	approximate
ASAT	aspartate aminotransferase
BBA	Biologische Bundesanstalt für Land- und Forstwirtschaft
bw	body weight
(not b.w.)	
c	centi- (x 10^{-2})
CA	Chemical Abstracts
CAS	Chemical Abstracts Services
CCPR	Codex Committee on Pesticide Residues
ChE	cholinesterase
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
EBDC	ethylenebis(dithiocarbamate)
EC	(1) emulsifiable concentrate
	(2) electron-capture [chromatographic detector]
ECD	electron-capture detector
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
FID	flame-ionization detector
FPD	flame-photometric detector
g (not gm)	gram
□g	microgram
GAP	good agricultural practice(s)
GC-MS	gas chromatography - mass spectrometry
G.I.	gastrointestinal
GL	guideline level

GLC	gas-liquid chromatography
GLP	Good Laboratory Practice
GPC	gel-permeation 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
IBT	Industrial Bio-Test Laboratories
i.d.	internal diameter
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 a WHO Expert Group on Pesticide Residues)
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
MFO	mixed function oxidase
□m	micrometre (micron)
min (not min.)	minute(s)
MLD	minimum lethal dose
M	molar
mo	month(s)

(not mth.)	
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
MTD	maximum tolerated dose
n	normal (defining isomeric configuration)
NCI	National Cancer Institute (United States)
NMR	nuclear magnetic resonance
NOAEL	no-observed-adverse-effect level
NOEL	no-observed-effect level
NP(D)	nitrogen-phosphorus (detector)
NTE	neuropathy target esterase
OP	organophosphorus pesticide
PHI	pre-harvest interval
ppm	parts per million. (Used only with reference to the concentration of a pesticide in an experimental diet. In all other contexts the terms mg/kg or mg/l are used).
PT	prothrombin time
PTT	partial thromboplastin time
PTU	propylenethiourea
RBC	red blood cell
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)
sp gr (not sp. gr.)	specific gravity
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
TPTA	triphenyltin acetate
TPTH	triphenyltin hydroxide
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
v/v	volume ratio (volume per volume)
WG	water-dispersible granule
WHO	World Health Organization
WP	wettable powder
wt/vol	weight per volume
w/w	weight ratio (weight per weight)
<	less than
≤	less than or equal to
>	greater than
≥	greater than or equal to
*	(following residue levels, e.g. 0.01* mg/kg): level at or about the limit of determination

INTRODUCTION

The report of the Joint Meeting of the FAO Panel of Experts on Pesticide Residues in Food and the Environment and the WHO Toxicological and Environmental Core Assessment Groups (JMPR), held in Geneva, 18-27 September 1995, 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 residue and toxicological considerations will be available. Special attention is drawn to Annex I containing updated ADIs, MRLs, and temporary ADIs and MRLs, which also appears in full as part of the report of the Meeting.

Some of the compounds considered at this 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 Codex Committee on Pesticide Residues (CCPR) however, a comprehensive 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 a double asterisk 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 1995 JMPR for the FAO Panel of Experts on Pesticide Residues in Food and the Environment:
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Note: Any comments on residues in food and their evaluation should be addressed to the:

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AZINPHOS-METHYL (002)

EXPLANATION

Azinphos-methyl was originally evaluated in 1965 and has been reviewed on several occasions since. In 1991 the JMPR required additional data by 1993 to support the CXL for grapes. These data were not available to the 1993 Meeting, which was informed that data from trials on grapes in Germany and Italy, including processing studies, would be available for the 1995 Meeting. In 1993 the CCPR recommended deletion of the CXL and it was subsequently deleted by the CAC.

At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis for almonds and wheat (ALINORM 95/24, para 68). Several delegations observed that the database was not sufficient to establish MRLs for wheat. The proposed MRLs for almond and wheat were held at step 7B pending the review of written comments by the JMPR.

METHODS OF RESIDUE ANALYSIS

Plant material. Samples of plant material are extracted with acetone and after filtration the extract is evaporated to an aqueous remainder. Following the addition of distilled water the extract is added to a solid phase extraction column and the column eluted with ethyl acetate. The ethyl acetate eluate is concentrated, dissolved in cyclohexane and cleaned up on a silica gel column. After transfer of the relevant solvent fractions into ethyl acetate determination is by GLC with an FPD. This method was also suitable for the determination of demeton-S-methylsulphon. Recovery data were provided for apples, pears, peaches, grapes, must, wine, sugar beet, nectarines and potatoes as given in Table 1. (Seym, 1992a,b).

Table 1. Analytical recoveries of azinphos-methyl.

Substrate	Recovery, %	RSD[1]	LOD (mg/kg)	Reference
Apple	83-104	not specified	0.04	(Seym, 1992a)
Pear	74-90	not specified	0.04	(Seym, 1992a)
Peach	84-100	not specified	0.04	(Seym, 1992a)
Grapes - bunch segment	73-103	RSD 13.2	0.04	(Seym, 1992b)
Grape - must	72-85	RSD 8.7[2]	0.04	(Seym, 1992b)
Grape - wine	100-106	RSD 11.9[2]	0.04	(Seym, 1992b)
Sugar beat - root	81-88	not specified	0.04	(Seym, 1992b)
Sugar beat - leaf	89-98	not specified	0.04	(Seym, 1992b)
Nectarine	87-105	not specified	0.04	(Seym, 1992b)
Potato	81-93	not specified	0.04	(Seym, 1992b)

[1] Relative standard deviation
[2] These values were taken from the Italian residue trials report. (Seym, 1993)

USE PATTERN

Extensive information on GAP for the use of azinphos-methyl was given in the 1991 monograph. Information provided to the present Meeting on additional or amended GAP is shown in Tables 2 and 3.

Table 2. Registered uses of azinphos-methyl for grapes. WP formulation.

Country	Application				PHI, days	Reference
	Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.		
Germany	spray	0.26-0.82	0.016-0.051	1	49	Germany, 1994
Italy	spray	0.3-0.7[1]	0.0375-0.05	2	20	Thomas, 1995
New Zealand	HV spray to run-off	up to 1.0	0.0375-0.05	6-9	14	Lunn, 1995

[1] Calculated on the basis of a stated water volume of 800-1400 l/ha

Table 3. Registered uses of azinphos-methyl for commodities other than grapes.

Crop	Country	Form	Application				PHI,	Ref.
			Method	Rate, kg ai/ha	Spray conc, kg ai/hl	No.	days	
Apple	Peru	EC	spray	0.4-1.5[1]	0.2-0.25	unspecified		Pastor Talledo, 1994
Apple and pear	Netherlands	WP	spray	0.375-0.56	0.0375	1-3[2]	21	Olthof, 1995
Apple and pear	Netherlands	WP[3]	spray	0.3-0.45	0.03	1-3[2]	21	Olthof, 1995
Apple and pear	New Zealand	WP	HV spray to run-off	up to 1.5	0.0375- 0.05	7-10	14	Lunn, 1995.
Potato	Netherlands	WP	spray	0.25	0.042-0.125[1]	1-2[2]	28	Olthof, 1995
Potato	Peru	EC	spray	0.375-1.2	0.25-0.4	unspecified		Pastor Talledo, 1994
Rice	Peru	EC	spray	1	0.4	unspecified		Pastor Talledo, 1994
Stone fruit - apricots, cherries, nectarines, Peaches & plums	New Zealand	WP	HV spray to run-off	up to 1.5	0.0375- 0.05	5-8	21 (Peach & apricot) 14 (other stone fruit)	Lunn, 1995.
Tomato	Peru	EC	spray	0.5	0.25	unspecified		Pastor Talledo, 1994

[1] Calculated from the water volume given
[2] Interval of 10 days between applications
[3] Formulation combined with propoxur

RESIDUES RESULTING FROM SUPERVISED TRIALS

Grapes. The 1991 monograph reported six US trials in which residues following treatment at 0.84 kg ai/ha were 0.22-3.37 mg/kg in samples taken 14 days after the last treatment. US GAP involves a maximum application rate of 1.1-1.2 kg ai/ha with a PHI of 10 days (WP) or 7 days (EC). The 1991 Meeting concluded that the additional residues data were insufficient to propose an amendment to the CXL which existed at that time.

Four new Italian supervised trials conducted according to Italian GAP (0.3-0.7 kg ai/ha) were available from the manufacturer. Residues were <0.04-0.61 mg/kg at the GAP PHI of 20 days as shown in Table 4.

Table 4. Residues in grapes from Italian supervised trials (1992).

Region	Application	Sample	Residues, mg/kg, after PHI,	Ref.

						days				
	Form	No.	kg ai/ha	kg ai/hl		0	7	15	20	
Ravenna	WP	2	0.5	0.05	grape[1]	0.41	0.35	0.10	<u><0.04</u>	Seym, 1993
					must	-	-	-	0.06	
					wine	-	-	-	<0.04	
Ravenna	WP	2	0.5	0.05	grape[1]	0.47	0.24	0.21	<u>0.07</u>	Seym, 1993
					must	-	-	-	0.09	
					wine	-	-	-	<0.04	
Bisceglie	WP	2	0.5	0.05	grape[1]	-	-	-	<u>0.61</u>	Seym, 1993
Andria	WP	2	0.5	0.05	grape[1]	-	-	-	<u>0.25</u>	Seym, 1993

Underlined results are from treatments according to GAP
[1] The laboratory samples consisted of "segments of bunches of grapes"

Data from residue trials on Brussels sprouts were submitted but have not been evaluated as part of this review (Olthof, 1995).

The new Italian trials indicate that the residues resulting from Italian GAP are likely to be lower than those resulting from US GAP.

<u>Wheat</u>. The 1991 JMPR recommended an MRL of 0.2 mg/kg for wheat, based on trials conducted in the USA. At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis for wheat and almonds. Information was supplied indicating that in older azinphos-methyl studies residue analyses of many crops, among them almonds and wheat, were carried out by a colorimetric method in which the hydrolysis product anthranilic acid was determined. The method was quite unspecific and other hydrolysis products were capable of interfering with the quantification of azinphos-methyl. The manufacturer has stated that "newer studies on both crops have been performed using more specific analytical methods. The results of these studies show that the residues detected are considerably lower then previously assumed." (Thomas, 1994).

Analyses in the US residue trials reported in the 1991 monograph with references M80093-80094, M80110-80113 and M80161 were by the older colorimetric method. The seven remaining residue trials with references M69585-69589 and M80955-80956 were with the new specific method of analysis.

In addition to the question about the method of analysis several delegations at the 1994 CCPR observed that the database was not sufficient to establish an MRL for wheat. Of the seven trials with the new specific method of analysis, samples were taken 34-38 days (1 trial), 48-52 days (2 trials), 59 days (1 trial) and 71-75 days (3 trials) after the final application. GAP has been reported for Canada and Mexico in which the recommended PHI is 30 days. Only one trial included a PHI (34-38 days) close to that of GAP, with residues of <0.02 and 0.2 mg/kg in the grain and straw respectively.

<u>Almonds</u>. The 1991 JMPR recommended an MRL of 0.3 mg/kg for almonds, based on trials conducted in the USA. At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis. Information supplied confirmed that the results obtained with the colorimetric method were unreliable (see wheat above).

Two series of trials were reported in the 1991 JMPR monograph. Trials with references M46359-46364, M52654-52655 and M66738-66739 used the older colorimetric method. Residues from these trials were reported as <0.10-0.21 mg/kg in the kernels and 0.72-8.24 mg/kg in the hulls. It is these trials which appear to have been used to support the MRL of 0.3 mg/kg.

The 24 trials in the 1991 monograph with report references M69959-69982 were with the new

specific method of analysis. Residues were reported as <0.02-0.04 mg/kg in the kernels and 0.04-3.65 mg/kg in the hulls. (Thomas, 1995b).

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were submitted.

In processing

Data were provided on the residues following the processing of grapes into must and wine as part of two of the Italian residue trials (see Table 4). When grapes containing residues of <0.04-0.07 mg/kg were processed the residues in must and wine were 0.06-0.09 and <0.04 mg/kg, respectively. However the experimental details of the processing were submitted too late for full consideration by the Meeting and were in the form of a draft translation (Seym, 1993).

Residues in the edible portion of food commodities

No data were submitted, but none would be required for grapes.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Results of random monitoring analyses undertaken by the Australian Department of Primary Industries and Energy between 1 January 1989 and 30 June 1992 are shown in Table 5. Sampling of fruit and vegetables was of the whole item, excluding stones, stems, crowns etc. (Coleman, 1995).

Table 5. Australian monitoring data for azinphos-methyl.

Commodity	Residue, mg/kg	Number of samples
grapes	<0.1	228
	0.1-0.4	1
	TOTAL	229
broccoli	<0.1	4
Brussels sprouts	<0.1	12
cabbage	<0.1	67
capsicum (peppers), whole	<0.1	3
carrot	<0.1	84
cauliflower	<0.1	70
celery	<0.1	8
citrus fruit	<0.1	88
cucumber	<0.1	20
dried tree fruits	<0.1	52
dried vine fruits	<0.1	98
Grapes, fresh	<0.1	248
lettuce, whole	<0.1	69
melons, whole	<0.1	20
nectarines, whole	<0.1	4
papaws	<0.1	6
Peaches	<0.1	8
Pears	<0.1	355
	trace only	3
	<0.1 - 0.4	7
	TOTAL	366
plums	<0.1	2
Potatoes	<0.1	112
pumpkin	<0.1	31
raspberry	<0.1	3
strawberry	<0.1	14
tomato	<0.1	43
zucchini	<0.1	22
onion, whole	<0.1	442

NATIONAL MAXIMUM RESIDUE LIMITS

Table 6. National MRLs for azinphos-methyl in grapes (Thomas, 1995).

Country	MRL (mg/kg)
Australia	2
Belgium	1
Canada	5
Chile	4
France	1
Germany	1
Greece	1
Italy	1
Kenya	4 (temporary)
Luxembourg	1

Country	MRL (mg/kg)
Malaysia	4
Mexico	5
Netherlands	1
Portugal	1
South Korea	1
Spain	1
Taiwan	0.5
Turkey	0.5
UK	2
USA	5

Coleman (1995) and Olthof (1995) reported the Australian and Netherlands national MRLs, respectively, for other commodities. These were the same as reported in the 1991 JMPR monograph and are not reproduced here.

APPRAISAL

Azinphos-methyl was originally evaluated in 1965 and has been reviewed on several occasions since. In 1991, the JMPR carried out an extensive re-evaluation and required additional data by 1993 to support the Codex maximum residue limit (CXL) for grapes. These data were not available to the 1993 Joint Meeting, which was informed that data from trials on grapes in Germany and Italy, including processing studies, would be available for the 1995 Meeting. In 1993 the CCPR recommended deletion of the CXL and it was subsequently deleted by the CAC.

At the 1994 CCPR, the delegation of Germany questioned the accuracy of the method of analysis for almonds and wheat (ALINORM 95/24, para 68). Several delegations observed that the data were not sufficient to establish an MRL for wheat. The proposed MRLs for almonds and wheat were held at step 7B pending the review of written comments by the JMPR.

An analytical method suitable for plant material was submitted together with validation data for a number of crops. Determination was by GLC with an FPD with a reported limit of determination of 0.04 mg/kg.

Information on GAP was supplied by Germany, Australia, New Zealand and the manufacturer. Information from Australia on monitoring analyses of a large number of commodities showed that residues were all below the limit of determination (<0.1 mg/kg) except in one grape sample of 229 (reported within the range 0.1-0.4 mg/kg), and seven pear samples of 366 (<0.1-0.4 mg/kg).

Grapes. The 1991 monograph reported six US trials, carried out in one season, in which residues following treatment at 0.84 kg ai/ha were 0.22-3.37 mg/kg in samples taken 14 days after the last treatment. GAP in the USA requires a maximum application rate of 1.1-1.2 kg ai/ha with a PHI of 10 days for WP and 7 days for EC. The 1991 Meeting concluded that the additional residues data were insufficient to propose amendment to the CXL of 4 mg/kg for grapes and that residues data from countries other than the USA were desirable.

New Italian supervised trials conducted according to Italian GAP were available from the manufacturer. Residues were <0.04-0.61 mg/kg at a PHI of 20 days. However only four trials were available, conducted at three locations. The Meeting agreed that the six US trials could not support a

recommendation because a combination of the low application rate and the longer PHI used in these trials might lead to an underestimate of the maximum residue, and concluded that the data were insufficient to recommend an MRL for such an important commodity. The Meeting was informed that the manufacturer was considering carrying out further trials on grapes in Southern Europe.

The new Italian trials indicate that the residues resulting from Italian GAP are likely to be lower than those resulting from US GAP.

Wheat. At the 1994 CCPR the delegation of Germany questioned the accuracy of the method of analysis used and the MRL of 0.2 mg/kg recommended by the 1991 JMPR. In addition, several delegations observed that the data were not sufficient to establish an MRL for wheat. Information was brought to the attention of the Meeting that indicated that the accuracy of the old colorimetric method of analysis used in some of these trials was inadequate. Although a new specific method of analysis was used in seven of the US wheat trials only one of the trials included results at the PHI reported as Canadian and Mexican GAP (30 days). In the other six trials the PHIs were 48-75 days. The Meeting recommended that the MRL for wheat should be withdrawn.

The 1991 JMPR had recommended the MRL for wheat to replace the CXL for cereal grains, which it concluded was not adequately supported.

Almonds. At the 1994 CCPR the delegation of Germany questioned the MRL of 0.3 mg/kg for almonds recommended by the 1991 JMPR. The Meeting was informed that the accuracy of the old colorimetric method of analysis used in some of these trials was inadequate. Data from two series of trials were presented in the 1991 JMPR monograph. Samples from the trials which appear to have been used to support the MRL of 0.3 mg/kg were analysed by the colorimetric method. In a further 24 US trials in which a new specific method of analysis was used, residues were reported as <0.02-0.04 mg/kg in the kernels and 0.04-3.65 mg/kg in the hulls. On the basis of these trials the Meeting estimated maximum residue levels of 0.05 mg/kg for almonds and 5 mg/kg for almond hulls.

When grapes containing residues of <0.04-0.07 mg/kg were processed the residues in must and wine were 0.06-0.09 and <0.04 mg/kg, respectively. However the details of the processing were submitted too late for full consideration by the Meeting and were in the form of a draft translation. The Meeting understood that the manufacturer had agreed to submit the original study report and the final translation containing the full experimental details to the FAO for future consideration by the FAO Panel.

RECOMMENDATIONS

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

Definition of the residue: azinphos-methyl

Commodity		Recommended MRL (mg/kg)		PHI on which based, days
CCN	Name	New[1]	Previous	
TN 0660	Almonds	0.05	0.3	28
AM 0660	Almond hulls	5	-	28
GC 0080	Cereal grain	W[2]	0.2	-
GC 0654	Wheat	W	0.2	-

[1] W: the previous recommendation is withdrawn
[2] This CXL had already been marked for deletion by the 1991 JMPR.

REFERENCES

Coleman, I. 1995. Commonwealth Department of Primary Industries and Energy, Australia. Personal Communication. 12 April 1995.

Germany, 1994. Submission by the Federal Biological Research Centre for Agriculture and Forestry, July 1994. Unpublished.

Lunn, D.W. 1995. Ministry of Agriculture and Fisheries, New Zealand. Personal Communication. 25 May 1995

Olthof, P.D.A, 1995. Directoraat-Generaal van de Volksgezondheid, Netherlands, 9 March 1995. Personal Communication.

Pastor Talledo, C. 1994. Direccion de hygiene, Alimentarius y Control de Zoonosis, Peru. Personal communication. 23 November 1994.

Seym, M. 1992a. Method for the gas chromatographic determination of residues of azinphos-methyl and demeton-S-methylsulfon in plant material. Method no. 00260, report no. RA-72/92. Bayer AG, Germany. Unpublished.

Seym, M. 1992b. Supplement to Method 00260 (grapes). Method no. 00260/E001. Bayer AG, Germany. Unpublished.

Seym, M. 1993. Determination of residues of Gusathion 25WP in/on grape under actual use conditions in Italy. report no. Bayer RA-2084/92, incl. BBA bulletins 0339-92, 0565-92 and 0567-92. Unpublished.

Thomas, J. 1994. Bayer AG. Personal communication to Dr W. Topner. 24 October 1994. Unpublished.

Thomas, J. 1995a. "Thomas, J./P-E/Reg RA" sent with personal communication from Bayer AG.. 24 February 1995. Unpublished.

Thomas, J. 1995b. Bayer AG. Personal communication. 18 July 1995. Unpublished.

BENTAZONE (172)

EXPLANATION

Bentazone was evaluated originally in 1991 (a minor correction to Annex I of the report was noted in 1992) and again in 1994. At the 27th (1995) Session of the CCPR the delegation of Germany, supported by France, drew attention to the residue definition for animal products. They preferred a definition which did not include metabolites, as in practice no residues of metabolites were found. These delegations were also of the opinion that the LOD was too low when metabolites were included in the residue definition for plant materials.

At the invitation of the Codex Secretariat comments were received from Germany, France and the USA. In addition the manufacturer submitted recent reports to clarify the residue situation. The new information is included in the present evaluation.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

The metabolism of bentazone, 6-hydroxybentazone and 8-hydroxybentazone was studied in lactating goats and hens.

One lactating goat (goat A) was dosed once a day with 3 mg ^{14}C-labelled active ingredient per kg body weight for 5 consecutive days, and a second goat (B) received 8 daily doses of 50 mg ai/kg bw. The dose levels correspond to 123 ppm and 1420 ppm in the feed respectively. The animals were slaughtered 24 and 4 hours after the final dose. Residue levels increased in the urine and faeces during the repeated administration of the compound. Most of the administered dose was eliminated in the urine (91.4% and 80.6%), while the faeces contained 0.6% and 5.6% respectively (BASF, 1990). The radioactivity extracted with methanol and water amounted to 98.5% from muscle, 98.1% from kidney, 95.9% from liver and 98% from fat. 90-100% of the residues in the milk were extractable with methanol. Most of the unextractable residues were released after incubation with pronase. The parent bentazone constituted about 71-96% of the total radioactive residues (TRR) in milk, 71-97% in muscle, 94-98% in fat, 91-98% in kidney, 83-84% in liver, 97-100% in urine and 71% in faeces. The bile and liver contained bentazone-*N*-glucuronide in addition to the parent compound. No 6-hydroxybentazone, 8-hydroxybentazone or AIBA (2-aminoisopropylbenzamide) could be found in the milk or tissues. Two minor metabolites at a concentration of 0.002 mg/kg bentazone equivalents were found in milk from the goat dosed at 3 mg/kg bw. The extractable residues measured in the milk and tissues are shown in Table 1 (BASF, 1991c).

Table 1. ^{14}C levels in the milk and tissues of lactating goats after dosing with 3 and 50 mg [^{14}C]bentazone/kg bw/day.

Sample	Residues, mg/kg, expressed as bentazone	
	3 mg/kg bw	50 mg/kg bw
Milk	0.029	0.29
Muscle	0.016	1.28
Fat	1.69[1]	2.85
Kidney	0.61	50.1
Liver	0.058	3.62

[1] Considered to be an outlier since it is not expected that bentazone, with a log P_{ow} of -0.45, would accumulate in fat

Two lactating goats were dosed with [^{14}C]6-hydroxybentazone at nominal dose levels of 2 mg/kg bw/day (goat A) and 40 mg/kg bw/day (goat B) corresponding to 41 ppm and 973 ppm in the feed. The single daily doses were administered for 5 and 6 consecutive days respectively. The animals were slaughtered 24 and 4 hours after the final dose. The proportions of the total administered dose excreted with the urine and faeces were 69.9% and 86.1% 4 and 24 hours after the last dose respectively (BASF, 1991a). The radioactive residues measured in various samples are shown in Table 2.

Metabolites produced by the high-dose goat were identified. In the milk, the main metabolite was identified as the sulfate of 6-hydroxybentazone (43% of the TRR), while 6-hydroxy-bentazone itself accounted for only 1%. In addition three minor metabolites were detected, each at about 5-6% of the TRR or 0.026-0.033 mg/kg bentazone equivalents. 6-hydroxybentazone was identified in the extracts of fat (94% of the TRR), kidney (73%), muscle (44%) and liver (44%). The proportion of conjugates amounted to 5% of the TRR in kidney, 7% in muscle, and 35% in liver. The liver conjugate was identified as the sulfate of 6-hydroxybentazone (BASF, 1995a). Urine and faeces contained mainly 6-hydroxybentazone.

A similar experiment was carried out with the administration of [^{14}C]8-hydroxybentazone. The doses were equivalent to 42 and 732 ppm in the feed. The proportions of the total administered dose excreted with the urine and faeces were 83.3% and 91.4% 24 hours after the final dose respectively (BASF, 1991b). The residues in the milk and tissues are shown in Table 2. The radioactivity in the urine and faeces consisted exclusively of 8-hydroxybentazone, whereas the residues in the bile included 62% of conjugates besides free 8-hydroxybentazone. Residues in the milk, muscle, fat, liver and kidneys were identified as unchanged 8-hydroxybentazone (29%, 61%, 82%, 75% and 95% of the TRR respectively) and conjugates thereof (41%, 21%, 5%, 11% and 3%; BASF, 1995b).

Table 2. Total radioactive residues in goat tissues and milk after administration of [^{14}C]6-hydroxy-bentazone and[^{14}C]8-hydroxybentazone.

Sample	TRR, mg/kg as hydroxybentazone, from			
	6-hydroxy, 41 ppm[1]	6-hydroxy, 973 ppm[1]	8-hydroxy, 42 ppm[1]	8-hydroxy, 732 ppm[1]
Milk	0.021	0.529	0.023	0.623
Muscle	0.011	0.24	0.012	0.581
Fat	0.027	0.948	0.007	0.396
Kidney	0.14	22.46	0.118	17.72
Liver	0.018	0.915	0.021	2.247

[1] Dosage expressed as equivalent level in feed

Samples from the three studies on goats described above were also analysed by a modified version of the “cold analytical procedure” (BASF, 1974). The results for milk and tissues, except liver, were in good agreement with the recoveries in fortification experiments. The low results for liver were explained by the presence of bentazone *N*-glucuronide. Methanol/HCl hydrolysis was found to be unsatisfactory for cleavage of the conjugates as it leads to the decomposition of the residues. Enzyme treatment was therefore used to release the conjugated residues.

Lactating goats were fed on a diet containing 15 ppm bentazone and 75 ppm 6-hydroxybentazone (low-level group) or 75 ppm bentazone and 150 ppm 6-hydroxybentazone (high - level group) for 21 days and were then placed on a residue-free diet. One animal from each group was slaughtered 22, 28 or 35 days after the commencement of dosing. Milk samples were collected on days 1, 7, 14, 21, 28 and 35 for analysis. Bentazone residues in all the milk samples were below the limit of determination (0.02 mg/kg). Residues of 6-hydroxybentazone from the low-dose group were <0.02 mg/kg in all samples but one (0.03 mg/kg on day 1) and the milk from the high-dose group contained residues in the range <0.02-0.07 mg/kg. No residue was detectable on the 7th day of the withdrawal period. Less than 0.1% of the applied 6-hydroxybentazone was transferred into the milk (BASF, 1981).

[^{14}C]bentazone, [^{14}C]6-hydroxybentazone and [^{14}C]8-hydroxybentazone were each administered orally to separate groups of 10 laying hens once daily for 5 days. The doses were 10 mg/hen/day, equivalent to feed containing about 100 ppm. Radioactivity was measured in the excreta and eggs from 5 hens of each group during the dosing period and up to 6 hours after the final dose, and in the tissues of all 10 hens of each group 6 hours after the final dose. The excretion of radioactivity was rapid. The mean proportions of the total cumulative dose recovered 6 hours after the final dose were 93.6% from the bentazone group, 90.2% from the 6-hydroxybentazone group and 93.1% from the 8-hydroxybentazone group. The mean concentrations of radioactivity were highest in the kidneys in all groups, followed by muscle, liver and whole blood.

After the administration of bentazone, the major radioactive component in extracts of liver, muscle, fat and eggs was the parent compound. Radioactivity in extracts of liver was associated with both bentazone (0.92 mg/kg) and its *N*-glucuronide conjugate (0.12 mg/kg). The excreta contained 45% of the total radioactive residue as bentazone, 12% as its *N*-glucuronide conjugate, and 15% as 6-hydroxybentazone.

After dosing with the 6-hydroxy- and 8-hydroxy- metabolites, the main residues in the excreta were the unchanged compounds and their glucuronide or sulfate conjugates.

The residues measured in eggs, muscle, fat and liver are shown in Table 3 (BASF, 1988).

Table 3. ^{14}C levels (expressed as mg/kg of the fed compound) in laying hens and eggs after dosing at 10 mg/bird/day with bentazone, 6-hydroxybentazone or 8-hydroxybentazone.

Sample	^{14}C, mg/kg equivalent of		
	Bentazone	6-hydroxy-B	8-hydroxy-B
Eggs (maximum)	0.15	0.023	0.029
Muscle (average)	0.39	0.032	0.023
Fat (average)	0.09	0.005	0.034
Liver	1.1	0.13	0.23

RESIDUES RESULTING FROM SUPERVISED TRIALS

The residues in crops found in supervised trials at recommended use rates are summarized in the 1991 and 1994 Evaluations.

The composition of residues in soya bean seed, forage and fodder was determined in 6 trials in two States of the USA (BASF, 1989). The summarized results are shown in Table 4.

Table 4. Residues of bentazone and its metabolites in soya bean seed, forage, hay, and fodder following two applications with 1.1 kg ai/ha.

Sample, PHI (days)	Residue range, ^{14}C as mg/kg bentazone and metabolite equivalents				Average total residue mg/kg[2]
	Bentazone	8-OH-bentazone	6-OH-bentazone	Total[1]	
Seed 78-119	<0.05	<0.05	<0.05	<0.05	<0.05 (N = 6)
Forage 24-38	<0.05-0.15	0.06-2.0	0.06-3.5	0.18-5.3	3.0-2.0 (N = 6)
Hay 36-53	<0.05-0.62	0.87-3.0	0.92-2.5	<2.2-5.9	3.3-1.5 (N = 6)
Fodder 78-119	<0.05-0.20	0.05-0.20	<0.05-0.39	<0.15-0.79	0.42-0.32 (N = 6)

[1] When none of the compounds exceeded 0.05 mg/kg of bentazone equivalents, the total is reported as <0.05 mg/kg
[2] Ranges are means at shortest and longest PHIs. When samples contained less than the LOD of one compound, its residue was assumed to equal its LOD in calculating the total residue and the mean

Residues in animal products

In the recent studies reviewed above the animals had been dosed at high levels to allow identification of metabolites. In order to estimate the expected maximum residue levels in animal products the feeding levels must be related to the maximum residues likely to occur following the use of bentazone according to GAP and to the typical composition of animal feeds.

The highest-residue diet for goats was calculated on the composition of cattle feed (EPA, 1982) assuming that goats consume the same feed as cattle in quantities proportional to their weights.

The highest national MRLs for bean forage (10 mg/kg), soya bean hay (8 mg/kg) and peppermint hay (4 mg/kg) are registered in the USA (BASF, 1995c). Taking into account the maximum percentage of these commodities in cattle feed (35%, 40% and 60% respectively)), a highest-residue diet was composited of 35% bean forage, 40% soya bean hay and 25% peppermint

hay. Since an average 550 kg cow consumes about 20 kg dry matter/day, the maximum daily intake can be calculated as follows. Dry feed contains 7 kg bean forage which is equivalent to 35 kg fresh material (20% dry matter, DM). This contains (35 kg x 10 mg/kg) = 350 mg residue. Similarly, the contributions of soya bean hay (DM = 86%) and peppermint hay (DM = 86%) to the intake of bentazone are 74.4 mg and 23.3 mg respectively. The total calculated maximum intake is about 448 mg/animal/day.

The residues in plants consist of bentazone, 6-hydroxybentazone and 8-hydroxybentazone. The hydroxy compounds need not be considered as residues in animal products because they are excreted rapidly by the animals and result in negligible residues. The proportions of the residue components, illustrated in the previous evaluations and in Table 4, vary with time and plant. For a maximum residue estimation a 1:1:1 ratio of bentazone and its two hydroxy metabolites can be assumed. Consequently the 448 mg total residue contains 149 mg bentazone which is equivalent to about 0.3 mg bentazone/kg bw/day. On the assumption of a similar intake for goats and cows, the goat A in the first metabolism study (p.??), given 3 mg/kg, was therefore overdosed by a factor of 10, and the goat B by a factor of 167 (50/0.3).

On the basis of the overdose factors, the calculated maximum residues in the edible products of goats are shown in Table 5.

The relatively high residues in the kidney and to a lesser extent in the liver of goat B can be attributed to the short interval between final dosing and slaughter, which is unlikely to occur in practice. The calculated residues in the liver and kidney of goat A therefore give a more realistic estimate of likely residues.

The factor for the overdosing of the hens in a maximum-residue situation can be calculated by assuming that the birds are eating only linseed (the highest national MRL is 1.5 mg/kg for the sum of bentazone and the two hydroxybentazones). The consumption by a 1.9 kg bird is 120 g feed. The factor for overdosing is 175. The corresponding residues are included in Table 5.

Table 5. Calculated bentazone levels in the milk and tissues of lactating goats, and the tissues and eggs of hens, from projected maximum intakes of residues in feed.

Sample	Goat A (slaughtered 24 after final dose)	Goat B (slaughtered 4 h after final dose)	Laying hens
Milk	0.003	0.002	-
Muscle	0.002	0.008	0.002 mean
Fat	0.17[1]	0.02	0.001 mean
Kidney	0.06	0.30-	-
Liver	0.006	0.02	0.006
Eggs	-	-	0.001 max.

[1] Considered to be an outlier since it is not expected that bentazone, with a log P_{ow} of -0.45, would accumulate in fat

METHODS OF RESIDUE ANALYSIS

The recent studies confirmed the applicability of the analytical procedure (BASF, 1974) described in the 1991 evaluation.

APPRAISAL

Bentazone was evaluated originally in 1991 and subsequently in 1992 and 1994. At the 27th Session of the CCPR the delegation of Germany, supported by France, suggested that residue definition for animal products should not include metabolites, as in practice no residues of metabolites were found. These delegations were also of the opinion that the LOD was too low when metabolites were included in the residue definition for plant materials.

Metabolism studies were conducted on goats and hens. In goats dosed at 3-50 mg ai/kg bw/day for 5 and 8 days, the parent bentazone constituted about 71-96% of the total radioactive residues (TRR) in the milk, 71-97% in muscle, 94-98% in fat, 91-98% in kidney, 83-84% in liver, 97-100% in the urine and 71% in faeces. The bile and liver contained bentazone *N*-glucuronide in addition to the parent compound. No 6-hydroxybentazone, 8-hydroxy-bentazone or AIBA (2-amino-*N*-isopropylbenzamide) could be found in the milk or tissues. When 6-hydroxybentazone and 8-hydroxybentazone were fed separately, residues were rapidly excreted (86.1% and 91.4% within 24 hours after the last dose respectively). The residues consisted mainly of 6-hydroxybentazone or 8-hydroxybentazone with smaller amounts of their glucuronide and sulfate conjugates.

In hens dosed at 10 mg ai/hen/day for 5 days, the major residue components were the parent bentazone and its glucuronide conjugate. No AIBA was detected.

Taking into consideration the highest residues which may occur in plant commodities and the composition of the feed of animals, it was concluded that the residues in meat, milks and eggs would not exceed the present draft MRLs of 0.05 mg/kg.

Since in the new studies no AIBA could be detected in any of the analysed tissues, milk, eggs or excreta even when extremely high doses were fed to goats and hens, the Meeting concluded that there was sufficient evidence to change the definition of the residues in animal products to bentazone alone. The change of the definition does not affect the estimated maximum residue level

(0.05* mg/kg) for meat, milks and eggs.

The Meeting also reconsidered the residue definition and the recommended limits for plant products. As the recommended maximum residue limits set at or about the limit of determination indicate undetectable residues, none of the residue components (bentazone, 6-hydroxybentazone and 8-hydroxybentazone) should be present in detectable concentration, and their LODs should not be summed. Each of the residue components can be determined individually with an LOD of <0.02 mg/kg. The LOD of 0.05* mg/kg therefore gives a 250% allowance for regulatory laboratories, where the analytical conditions might not be optimized as well as in laboratories specialized in the analysis of these compounds.

The Meeting therefore confirmed its previous recommendations for plant commodities.

RECOMMENDATIONS

In the light of the new animal metabolism studies the Meeting recommended a change in the definition of the residue in animal products.

Definition of the residue in animal products: bentazone

REFERENCES

BASF, 1974. Determination of bentazone and AIBA residues in cow and chicken tissue. BASF 74/5086. Unpublished.

BASF, 1981. Residues of bentazone and 6-hydroxybentazone in milk following dietary administration to lactating goats. BASF 81/10068. Unpublished.

BASF, 1988. The metabolism of ^{14}C-bentazone and its hydroxylated metabolites in hens. BASF 88/0432. Unpublished.

BASF, 1989. Magnitude of residues of bentazone and metabolites in soybean seed, forage, hay and fodder. BASF 89/5046. Unpublished.

BASF, 1990. Dosing of lactating goats with ^{14}C-bentazone (BAS 351 H). BASF 90/10351. Unpublished.

BASF, 1991a. Dosing of lactating goats with ^{14}C-6-OH-bentazone for the isolation and identification of metabolites. BASF 91/10702. Unpublished.

BASF, 1991b. Dosing of lactating goats with ^{14}C-8-OH-bentazone for the isolation and identification of metabolites. BASF 91/10703. Unpublished.

BASF, 1991c. The metabolism of ^{14}C-bentazone (BAS 351 H) in lactating goats. BASF 91/11137. Unpublished.

BASF, 1995a. The metabolism of ^{14}C-6-OH-bentazone in lactating goats. BASF 95/10011. Unpublished.

BASF, 1995b. The metabolism of ^{14}C-8-OH-bentazone in lactating goats. BASF 95/10062. Unpublished.

BASF, 1995c. Working paper prepared for 1995 JMPR. Unpublished.

EPA, 1982. Pesticide Assessment Guidelines, Subdivision O: Residue Chemistry. Unpublished.

BIFENTHRIN (178)

EXPLANATION

Bifenthrin was first evaluated at the 1992 JMPR and MRLs were estimated for cereals, fruits, potatoes, hops, animal feeds and animal commodities. MRLs of 0.05* mg/kg were recommended for barley, maize and wheat to cover field application. Information has now been made available on the use of bifenthrin as a grain protectant on stored grain.

At the 26th (1994) Session of the CCPR (ALINORM 95/24, para 295) the Delegations of Germany and France considered that the available data on dry hops were inadequate for the proposed MRL. Additional explanatory notes on bifenthrin residue trials on hops have now been made available to the Meeting. Details of recent supervised trials on hops in the UK have also been supplied.

Information on registered uses of bifenthrin in the UK was made available to the Meeting.

METHODS OF RESIDUE ANALYSIS

Burden (1994) described a residue analytical method for bifenthrin and malathion in cereal grains and milling and baking products. The method relies on acetone extraction followed by solvent partition and column chromatography for clean-up and GLC with an ECD for quantitative analysis. The method was capable of determining bifenthrin and malathion simultaneously. The LOD for both compounds was stated to be 0.01 mg/kg, but no recovery data were available at this level on the cereal substrates. No information was available on the extraction efficiency of acetone for aged bifenthrin residues.

Analytical recoveries of added bifenthrin were grain 93-107% (15 samples), bran 92 and 99%, white flour 109%, wholemeal flour 104%, white bread 96% and wholemeal bread 101%. Recoveries were determined at concentrations of 0.1-0.4 mg/kg in grain, 0.3 and 20 mg/kg in bran, and 0.3 mg/kg in white flour, wholemeal flour, white bread and wholemeal bread.

Kennedy (1994) used a similar method for the analysis of hops. Analytical recoveries of 67-113% were achieved from spiked samples (11) over the concentration range 0.01 mg/kg to 10 mg/kg. The limit of determination was 0.01 mg/kg.

USE PATTERN

Bifenthrin is a pyrethroid insecticide particularly effective against Bostricid beetles (*Prostephanus truncatus* and *Rhyzopertha dominica*), but will also control *Sitophilus spp, Oryzaephilus spp*, and other insect pests. Proposed and registered uses of bifenthrin as a grain protectant are listed in Table 1. Registered uses of bifenthrin in the UK are listed in Table 2.

Table 1. Uses of bifenthrin as a protectant for stored grain.

Country	Form.	Application rate			
		bifenthrin, g/l	malathion, g/l	bifenthrin, g ai/t	malathion, g ai/t
Belgium	EC	20	400	0.3	6
Belgium	UL	7.5	150	0.3	6
Brazil[1]	EC	25 g/l bifenthrin + 125 g/l piperonyl butoxide		0.4	
France[1]	EC	20	400	0.3	6
France[1]	UL	7.5	150	0.3	6
Morocco[1]	EC	20	400	0.3	6
Morocco[1]	UL	7.5	150	0.3	6
Poland[1]	EC	20	400	0.3-0.4	6-8
Poland[1]	UL	7.5	150	0.3-0.4	6-8
UK[1]	EC	20	400	0.3	6
UK[1]	UL	7.5	150	0.3	6

[1] Proposed registration

The label and proposed labels also carry instructions for the treatment of grain stores 3-4 weeks before filling. The formulation is applied at the rate of 2.5 g bifenthrin per 100 m^2 of surfaces within the store.

Table 2. Registered uses of bifenthrin in the UK. All EC foliar applications.

Crop	Application			PHI, days
	Rate per applic., kg ai/ha	Spray conc, kg ai/hl	No.	
Apple	0.05	0.01	2	14
Barley, winter	0.0062	0.0015-0.003	2	60
Broccoli	0.0075	0.0012-0.0024	2	1
Brussels sprouts	0.0075	0.0012-0.0024	2	1
Cabbage	0.0075	0.0012-0.0024	2	1
Calabrese	0.0075	0.0012-0.0024	2	1
Cauliflower	0.0075	0.0012-0.0024	2	1
Hops	0.014-0.09	0.004	5	10
Linseed	0.0075	0.0018-0.0036	2	115
Oats, winter	0.0062	0.0015-0.003	2	60
Pear	0.05	0.01	2	14
Peas	0.0075	0.0018-0.0036	2	3
Rape, winter oilseed	0.0075	0.0018-0.0036	2	150
Rye	0.0062	0.0015-0.003	2	60
Strawberries	0.024-0.04	0.004	2	14
Triticale	0.0062	0.0015-0.003	2	60
Wheat, durum	0.0062	0.0015-0.003	2	60
Wheat, winter	0.0062	0.0015-0.003	2	60

In the USA bifenthrin is used on hops to control hop aphid and two-spotted spider mite. It is applied as a high-volume spray up to 3 times at a concentration of 0.0033 kg ai/hl and a rate of 0.1 kg ai/ha. The PHI is 14 days.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Kennedy (1994) reported on the bifenthrin residues in dried hops resulting from the application of bifenthrin in supervised field trials in the UK. The data are summarised in Table 3. Harrison and Owen (1994) used plot sizes of 5 or 6 rows of 15 m of hops in the trials. The hops were treated 5 times to run-off in high-volume applications. Two of the trials were in Kent and three in the West Midlands.

Table 3. Residues of bifenthrin in dried hops from high-volume foliar application of 5 x 0.004 kg ai/l EC in supervised trials in the UK in 1993 (Kennedy 1994).

Variety	Day	Residues, mg/kg	Ref.
Challenger	0 7	5.5 c1.4 5.1 c0.10	FCC 0693
Target	0 7	4.6 c<0.01 2.6 c<0.01	FCC 0693
Target	0 7	6.2 c0.03 5.5 c0.05	FCC 0693
Challenger	0 7	6.8 c1.1 4.5 c0.65	FCC 0693
Yeoman	0 7	5.3 c0.02 4.1 c0.01	FCC 0693

c: control sample

Residue data from supervised trials on hops in Germany were recorded in the 1992 Residue Evaluations. Additional explanatory notes have now been provided and the same data are presented in more detail in Table 4.

Table 4. Residues of bifenthrin in dried hops from EC foliar application of EC in supervised trials in Germany. Data were previously summarized in Table 5 of the 1992 bifenthrin residue evaluation. Underlined residues are from treatments according to UK GAP.

Year (variety)	Application			Day	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl	No.			
1984 (Tettnanger Früh-hopfen)	1×0.09 +4×0.15	0.003	5	0 3 5 7 10	3.6 2.1 0.5 1.2 <u>1.9</u>	008334 73/44
1984 (Northern Brewer)	1×0.09 +4×0.15	0.003	5	0 3 5 7 10	4.8 3.1 2.5 1.8 <u>1.9</u>	008335 73/44
1984 (Spalter)	1×0.09 +4×0.15	0.003	5	0 3 5 7 10	6.4 7.2 4.1 4.9 <u>2.9</u>	008336 73/44
1984 (Hersbrucker Spät)	1×0.09 +4×0.15	0.003	5	0 3 5 7 10	0.7 0.3 2.0 0.3 <u>0.7</u>	008337 73/44
1985 (Spalter)	1×0.075 +3×0.13	0.0025	4	0 3 5 7 10	2.2 4.0 2.5 1.4 <u>0.9</u>	008419 73/52
1985 (Hersbrucker Spät)	1×0.075 +3×0.13	0.0025	4	0 3 5 7 10	2.8 2.7 1.5 1.1 <u>4.2</u>	008420 73/52

Year (variety)	Application			Day	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl	No.			
1985 (Northern Brewer)	1×0.075 +3×0.13	0.0025	4	0 3 5 7 10	8.2 1.5 9.0 8.1 0.1	008421 73/52
1985 (Tettnanger Früh-hopfen)	1×0.075 +3×0.13	0.0025	4	0 3 5 7 10	2.3 2.5 1.6 1.5 1.8	008422 73/52
1987 (Golden Brewer)	2×0.075 +3×0.13	0.0025	5	0 3 5 7 10 7 10	g2.8 c0.13 g1.7 c0.16 g1.6 c0.13 g0.94 c0.09 g1.6 c0.55 1.6 c0.90 2.7 c1.2	DOW 02084 73/72B
1987 (Golden Brewer)	2×0.075 +3×0.13	0.0038	5	0 3 5 7 10 7 10	g3.1 c0.61 g1.9 c0.57 g1.4 c0.49 g0.90 c0.59 g1.6 c0.89 1.6 c0.60 2.5 c1.3	DOW 02085 73/72B
1987 (Northern Brewer)	2×0.075 +3×0.13	0.0025	5	0 3 5 7 10 7 10	g1.2 g0.92 g0.50 g0.92 g0.28 2.1 1.0	DOW 02086 73/72B
1987 (Northern Brewer)	2×0.075 +3×0.13	0.0038	5	0 3 5 7 10 7 10	g1.4 g0.59 g1.3 g0.79 g1.1 2.3 1.9	DOW 02087 73/72B

g: green hops. c: control sample

Haubruge *et al*. (1994) in Belgium treated grain (50 kg batches) by spraying and mixing in a cement mixer. Grain was then stored in mini-silos in a room where the temperature and humidity were not strictly controlled, but were measured. Temperatures were in the range 14.4 to 19.8°C, with grain moistures between 13.1% and 16.0%. Grain samples (200 g) were withdrawn at intervals and held at -18°C until analysis.

Binns *et al.* (1994) treated wheat (batches of 50 kg) with bifenthrin or a bifenthrin/malathion mixture in a cement mixer and then stored the treated grain at 20°C at ambient humidity in the UK. After various storage intervals samples (1.2 kg) were withdrawn for chemical analysis and at the 1-month and 3-month intervals samples of 3 kg were sent to a milling and baking laboratory.

Harrison and Derbyshire (1994) in the UK applied bifenthrin and malathion to barley grain, variety Marinka, moving down a chute into a grain store. The grain moisture was in the range 13% to 15%.

Table 5. Residues of bifenthrin and malathion resulting from supervised trials on stored grain after post-harvest applications. All 1992.

Country	Grain weight, temp	Form	Treatment, g ai/t	Storage time	Residues, mg/kg		Reference
					Bifenthrin	Malathion	
BARLEY							
UK	1 tonne	EC	b 0.4 + m 8.0	1 day 1 month 3 months 6 months 12 months	0.30 0.32 0.31 0.28 0.26	4.6 3.3 2.0 0.78 0.25	AK/2020/FM
UK	25-50 kg	EC	b 0.3 + m 6.0	1 day 1 month 3 months 6 months 12 months	0.22 0.22 0.29 0.24 0.19	3.0 2.4 1.9 0.42 0.20	AK/2020/FM
WHEAT							
Belgium	50 kg 15-20°C	UL	b 0.3 + m 6.0	1 day 1 month 3 months 6 months 12 months	0.18 0.17 0.22 0.14 0.16	4.4 4.8 2.1 0.86 0.69	11
Belgium	50 kg 15-20°C	EC	b 0.3 + m 6.0	1 day 1 month 3 months 6 months 12 months	0.18 0.19 0.14 0.15 0.15	3.8 3.6 1.9 0.35 0.62	11
Belgium	50 kg 15-20°C	UL	b 0.3 + m 6.0	1 day 1 month 3 months 6 months 12 months	0.23 0.23 0.24 0.14 0.19	5.5 2.3 2.1 1.1 0.79	11
Belgium	50 kg 15-20°C	EC	b 0.3 + m 6.0	1 day 1 month	0.23 0.16	6.3 4.2	11

Country	Grain weight, temp	Form	Treatment, g ai/t	Storage time	Residues, mg/kg		Reference
					Bifenthrin	Malathion	
				3 months	<0.01 [1]	0.12 [1]	
				6 months	0.25	0.83	
				12 months	0.12	0.50	
France (Us)	25-50 kg	UL	b 0.3 + m 6.0	1 day	0.23	3.5	73/89-1012
				1 month	0.22	2.2	CSL
				3 months	0.23	1.9	
				6 months	0.22	1.2	
				12 months	0.26	1.0	
France (Us)	25-50 kg	EC	b 0.3 + m 6.0	1 day	0.24	3.6	73/89-1012
				1 month	0.20	2.4	CSL
				3 months	0.21	1.8	
				6 months	0.21	0.9	
				12 months	0.19	0.29	
UK	25 kg 20°C	EC	b 0.5	1 day	0.37		AB09
				1 month	0.39		
				3 months	0.38		
				6 months	0.39		
				12 months	0.40		
UK	25 kg 20°C	EC	b 0.3 + m 6.0	1 day	0.25	3.8	AB09
				1 month	0.26	2.5	
				3 months	0.24	1.8	
				6 months	0.27	1.2	
				12 months	0.22	0.53	
UK	25 kg 20°C	UL	b 0.3 + m 6.0	1 day	0.26	3.5	AB09
				1 month	0.23	2.4	
				3 months	0.25	2	
				6 months	0.28	1.4	
				12 months	0.24	0.82	

b: bifenthrin m: malathion
[1] sample possibly interchanged with control sample

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware that the following MRL had been established.

Country	MRL, mg/kg	Commodity
Belgium	0.5	Stored grain

FATE OF RESIDUES IN STORAGE AND PROCESSING

Baxter (1995), in a laboratory-scale experiment, reported on the fate of bifenthrin and malathion during the malting of treated barley. Barley (batches of 350 g) treated at twice the recommended rate with bifenthrin and malathion was malted and the malts analysed for residues. Residues of bifenthrin in the barley and malt were 0.31 mg/kg and 0.026 mg/kg respectively; residues of malathion in the barley and malt were 4.6 mg/kg and not detected (<0.02 mg/kg) respectively. Information on the treatment rates, storage intervals before malting and the residue levels on the barley were not provided.

APPRAISAL

Bifenthrin was first evaluated at the 1992 JMPR and MRLs of 0.05* mg/kg were recommended for barley, maize and wheat to cover field applications. Information has now been made available on the use of bifenthrin as a grain protectant on stored grain.

At the 26th Session of the CCPR (ALINORM 95/24, 1994, para 295) the delegations of Germany and France considered that the available data on dry hops were inadequate for the proposed MRL. Additional explanatory notes on bifenthrin residue trials on hops have now been made available to the Meeting. Details of recent supervised trials on hops in the UK have also been supplied.

The residue analytical method for bifenthrin in cereal grains and milling and baking products relies on acetone extraction followed by solvent partition and column chromatography for clean-up and GLC with ECD for quantitative analysis. Good analytical recoveries were achieved for bifenthrin on grain (0.1-0.4 mg/kg), bran (0.3 and 20 mg/kg) and white flour, wholemeal flour and white bread (all 0.3 mg/kg).

A similar method was used for the analysis of hops where analytical recoveries of 67-113% were achieved for 11 spiked samples over the concentration range 0.01 mg/kg to 10 mg/kg. The limit of determination was 0.01 mg/kg.

In the UK registered use bifenthrin may be applied 5 times to hops at a spray concentration of 0.004 kg ai/hl. The hops may be harvested 10 days after the final application. The hops in the UK supervised trials were harvested 7 days after the final application, which was not strictly within GAP. However, the Meeting regarded the results as being consistent with the data from the German trials and as providing additional support.

The Meeting was informed that a registration for the use of bifenthrin on hops would not be pursued for the time being in Germany. The Meeting noted that the German residues data for dried hops, where bifenthrin spray concentrations were 0.0025-0.0038 kg ai/hl and the hops were harvested 10 days after the final application, were within UK GAP and re-evaluated the data according to UK GAP. Residues on dried hops at 10 days PHI in the 12 trials were 0.1, 0.7, 0.9, 1.0, 1.8, 1.9, 1.9, 1.9, 2.5, 2.7, 2.9 and 4.2 mg/kg.

The US use pattern on hops was reported in the 1992 JMPR Residue Evaluations as pending. The US trial data on hops reported in the 1992 Evaluations were evaluated against US GAP for hops reported to the current Meeting (3 applications, 0.1 kg ai/ha, spray concentration 0.0033 kg ai/hl and 14 days PHI). Residues in dried hops in the eight US trials were 0.5, 0.5, 0.7, 0.9, 1, 5, 5 and 5 mg/kg. Residues in dried hops from the same trials harvested 28 days after the final application also ranged up to 5 mg/kg.

Bifenthrin residues in dried hops from the total of twenty trials in the USA and Germany were 0.1, 0.5 (2), 0.7 (2), 0.9 (2), 1.0 (2), 1.8, 1.9 (3), 2.5, 2.7, 2.9, 4.2, and 5 (3) mg/kg. With a number of residues from supervised trials at 5 mg/kg, it is likely that in commercial practice residues in excess of 5 mg/kg will occur. The Meeting agreed that the data supported the current recommendation of 10 mg/kg for bifenthrin in dried hops.

Bifenthrin is effective as a grain protectant. It is registered in combination with malathion for use on stored grain in Belgium, and is proposed for registration in Brazil, France, Morocco, Poland and the UK. Bifenthrin is to be used at 0.3-0.4 g ai/t in combination with malathion at 6-8 g ai/t.

Storage experiments on barley in the UK and on wheat in Belgium, France and the UK showed that bifenthrin residues are stable for 12 months on stored grain at 20°C. Other pyrethroid grain

protectants have shown similar persistence. The levels of bifenthrin on the grain at the beginning and end of storage will essentially be the same.

The Meeting was reluctant to proceed with a recommendation for cereals until a number of points had been clarified. Information is needed on the efficiency of extraction of aged residues, national MRLs covering use on stored grains, and the fate of bifenthrin residues during commercial milling, baking and malting. Information should also be provided when proposed registrations become official or when new registrations for grain protectant uses are obtained.

FURTHER WORK OR INFORMATION

Desirable

1. Information on the efficiency of extraction by acetone of aged bifenthrin residues on stored grain. Acetone extraction is the first step in the analytical method.

2. Information on national MRLs for bifenthrin relating to uses on stored grains.

3. Information on the fate of bifenthrin during the commercial milling of wheat treated with it post-harvest. The studies should simulate commercial practices, including the effects of commercial cleaning.

4. Information on the fate of bifenthrin during the baking of bread.

5. Information on the fate of bifenthrin during the commercial malting of barley treated with it post-harvest. The studies should simulate the commercial process.

REFERENCES

Baxter, E.D. 1995. Pesticide trial MP 177: grain protectant. BRF International, UK. Unpublished.

Benwell, L. 1994. Bifenthrin and malathion: the determination of residues in grain and milling/baking products. Report 73/103-1012. Hazleton Europe, UK. Unpublished.

Binns, T.J., 6Buckland, A. and Tamsett, S. 1994. An assessment of the residues of 3 pesticide formulations applied to wheat. Report AB09. Central Science Laboratory, UK. Unpublished.

Burden, A.N. 1994. Bifenthrin and malathion: the determination of residues in grain and milling/baking products. Report 73/89-1012. Hazleton Europe, UK. Unpublished.

Harrison, C. and Derbyshire, R. 1994. Study to generate crop samples for residue analysis following treatment with a formulated bifenthrin/malathion product (ECH 92465). Final report on project AK/2020/FM. Agrisearch, UK. Unpublished.

Harrison, C. and Owen, J. 1994. Programme to generate crop samples for residue analysis following treatment of hops with Talstar 10 EC. Final report on project AK/2242/FM. Agrisearch UK Ltd. Unpublished.

Haubruge, E., Letellier, C. and Gaspar, C. 1994. Long-term effects of a bifenthrin/malathion insecticide: small bin tests. Report no. 11. Faculty of Agricultural Sciences, Belgium. Unpublished.

Kennedy, E.M. 1994. The determination of concentrations of bifenthrin in hops. Study no. FCC 0693. Restec Laboratories Limited. Unpublished.

BUPROFEZIN (173)

EXPLANATION

Buprofezin was first evaluated by the 1991 JMPR, which allocated an ADI of 0-0.01 mg/kg bw and recommended TMRLs for cucumber, tomato and oranges with 8 required and 4 desirable items of further work or information. Review was postponed at the request of the manufacturer until 1995, with the likely prospect of withdrawal of the TMRLs if analytical data were not available. The Meeting received and reviewed submissions intended to provide most of the required information.

METABOLISM AND ENVIRONMENTAL FATE

The 1991 JMPR monograph described the fate of residues in animals, plants, soil, water and water/sediment systems and listed the structures of buprofezin metabolites and related compounds. In response to requirements of the 1991 JMPR additional information was provided to the present Meeting on metabolism in animals and plants and fate in water (hydrolysis).

Animal metabolism

The 1991 JMPR reviewed metabolism studies on rats and chickens. It noted that these studies suggested that hydroxylation of the phenyl ring, oxidation at the sulfur atom and cleavage of the thiadiazinane ring are the major routes of metabolism. However, it concluded that on the basis of these studies alone the fate of residues in animals was not adequately understood and required submission of a ruminant metabolism study. The present Meeting received a study of metabolism in a cow (Haung and Smith, 1995), reportedly conducted according to US GLP.

A 420 kg lactating Jersey cow was dosed orally by gelatin capsules twice daily (after the morning and evening milkings) at a daily rate of 163 mg [^{14}C]buprofezin uniformly labelled in the phenyl ring (equivalent to 24.4 ppm wet weight or 26.6 ppm dry weight in the diet, or 0.38 mg/kg bw). Milk, urine and faeces were collected twice daily during treatment, and liver, kidney, muscle, fat and blood were collected after slaughter 15 hours after the last dosing. Samples were shipped frozen the same day to the test facility where they were kept frozen until analysis.

Samples were subjected to a number of extraction, hydrolysis and partitioning steps for analysis. For example liver, kidney and muscle samples were lyophilized and Soxhlet-extracted sequentially with solvents of increasing polarity (hexane, acetonitrile, ethanol and water). Organic and aqueous extracts were incubated with ß-glucuronidase and sulfatase before chromatography. Liver and kidney solids remaining after the exhaustive extraction ("bound" residues above 0.05 mg/kg) were subjected to acid (0.1M HCl) then base (0.1 M NaOH) hydrolysis, followed sequentially by incubations with proteinase, glucuronidase and 6 M HCl. These treatments released respectively 2.1%, 7.7%, 36.2%, 1%, and 6.7% of the ^{14}C in the liver. It can be seen that the proteinase released the highest proportion of the bound residue.

Samples were subjected to liquid scintillation counting and combustion analysis to determine the distribution of residues. Components of the residues were identified by TLC (normal, reverse-phase, and two-dimensional) and HPLC; separated fractions were compared with reference standards of known and likely metabolites (not including the thiobiuret derivative formed by hydrolysis).

The distribution of total ^{14}C- residues, expressed as buprofezin equivalents, is shown in Table 1.

Table 1. Distribution of ^{14}C residues in a cow dosed with [^{14}C]buprofezin (Haung and Smith, 1995).

Sample	^{14}C distribution		^{14}C in extract			
			hexane[4]	CH_3CN + EtOH	aqueous	unextractable
	mg/kg as buprofezin	% of total dose	% of total in sample (mg/kg[5])	% of total in sample (mg/kg[5])	% of total in sample (mg/kg[5])	% of total in sample (mg/kg[5])
Liver	1.21	0.66	0.02 (<0.001)	29.2 (0.35)	15 (0.18)	55 (0.66)
Kidney	0.41	0.04	0.002 (<0.001)	43.9 (0.18)	26.8 (0.11)	30 (0.12)
Muscle	0.018	0.24	--	44.4 (0.008)	16.7 (0.003)	44.4 (0.008)
Milk	0.028[1]	0.087	0.004 (<0.001)	42.9 (0.012)	28.6 (0.008)	21.4 (0.006)
Fat	0.02	0.15	0.15 (<0.001)	55 (0.01)	5 (0.001)	25 (0.005)
Blood	0.23	0.49	--	--	--	--
Faeces	5.4-12[2]	45.56	--	--	--	--
Urine	4.9-10.5[3]	18.84	--	--	--	--

[1] Highest level reached in whole milk (day 5 at plateau). Residues in cream about 1.5 times those in skimmed milk
[2] After day 3
[3] After day 2
[4] Residue in hexane after back wash with ethanol/water or acetonitrile
[5] Expressed as buprofezin

The distribution of identified and characterized metabolites is shown in Table 2.

Table 2. Identified and characterized compounds[1] in milk, tissues and excreta of a cow dosed with [^{14}C]buprofezin (Huang and Smith, 1995).

Sample	buprofezin	BF-9 = J ("Dione")	BF-2 = B		BF-12 = G		BF-13 = H		BF-23 = L		Largest unknown	
	% of TRR[2]	% of TRR	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR	mg/kg	% of TRR (no. of unknowns)	mg/kg
Liver	ND[3]		10.9	0.13[4]	3.5	0.042	2.5	0.030	2.2	0.027	5.9 (16)	0.07
Kidney	ND		18	0.074	3.9	0.016	3.1	0.013	7.7	0.032	4.5 (8)	0.02
Milk	ND		1	<0.001	2.1	0.001	2.6	<0.001	9.2	0.003	4.9 (6)	0.001
Faeces	12.6		48.4		--	--	--	--	--	--	11 (2)	
Urine 30 after min. reflux[5]	--	--	--	--	16.6		--	--	4.9		9	--
Urine after overnight digest[6]	--	1.3	7.7		14.5		5.4		6.4		13 (6)	

[1] Identification:

1991 monograph code	Huang and Smith code	Chemical name
B	BF-2	2-tert-butylimino-5-(4-hydroxyphenyl)-3-isopropyl-1,3,5,thiadiazinan-4-one
G	BF-12	1-isopropyl-3-phenylurea
H	BF-13	1-(4-hydroxyphenyl)-3-isopropylurea
J	BF-9	3-isopropyl-5-phenyl-1,3,5-thiadiazinan-2,4-dione
L	BF-23	N-(4-hydroxyphenyl)acetamide

[2] Total radioactive residue
[3] Not detectable

[4] Calculation: 1.2 mg/kg from Table 1 x 10.9% TRR in liver = 0.13 mg/kg
[5] In 0.5M/HCl
[5] In dioxane/HCl 50°C

These findings led the author to propose the metabolic profile for buprofezin in ruminants presented in Figure 1 and confirmed the metabolic profile proposed for animals in the 1991 monograph, which is repeated for reference in Figure 2. The structures in Figures 1 and 2 are identified in the list below.

Identification codes, chemical names, and common or trivial names of compounds in Figure 1 and Figure 2

Code used in Fig. 1	Code use in Fig. 2 & Fig. 1 of 1991 monograph	Chemical, common and trivial names
BF-1	A	buprofezin
BF-2	B	2-*tert*-butylimino-5-(4-hydroxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one ("*p*-hydroxybuprofezin")
	C	2-*tert*-butylimino-5-(3,4-dihydroxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one
	D	2-*tert*-butylimino-5-(4-hydroxy-3-methoxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one
BF-10	E	2-*tert*-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one 1-oxide (buprofezin oxide)
BF-11	F	1-*tert*-butyl-3-isopropyl-5-phenylbiuret
BF-12	G	1-isopropyl-3-phenylurea (IPU)
BF-13	H	1-(4-hydroxyphenyl)-3-isopropylurea (hydroxy-IPU)
BF-9	-[1]	3-isopropyl-5-phenyl-1,3,5-thiadiazinane-2,4-dione (the "dione")
	K	4-aminophenol (*p*-aminophenol)
BF-23	L	*N*-(4-hydroxyphenyl)acetamide

Figure 1. Metabolic profile of buprofezin in ruminants.

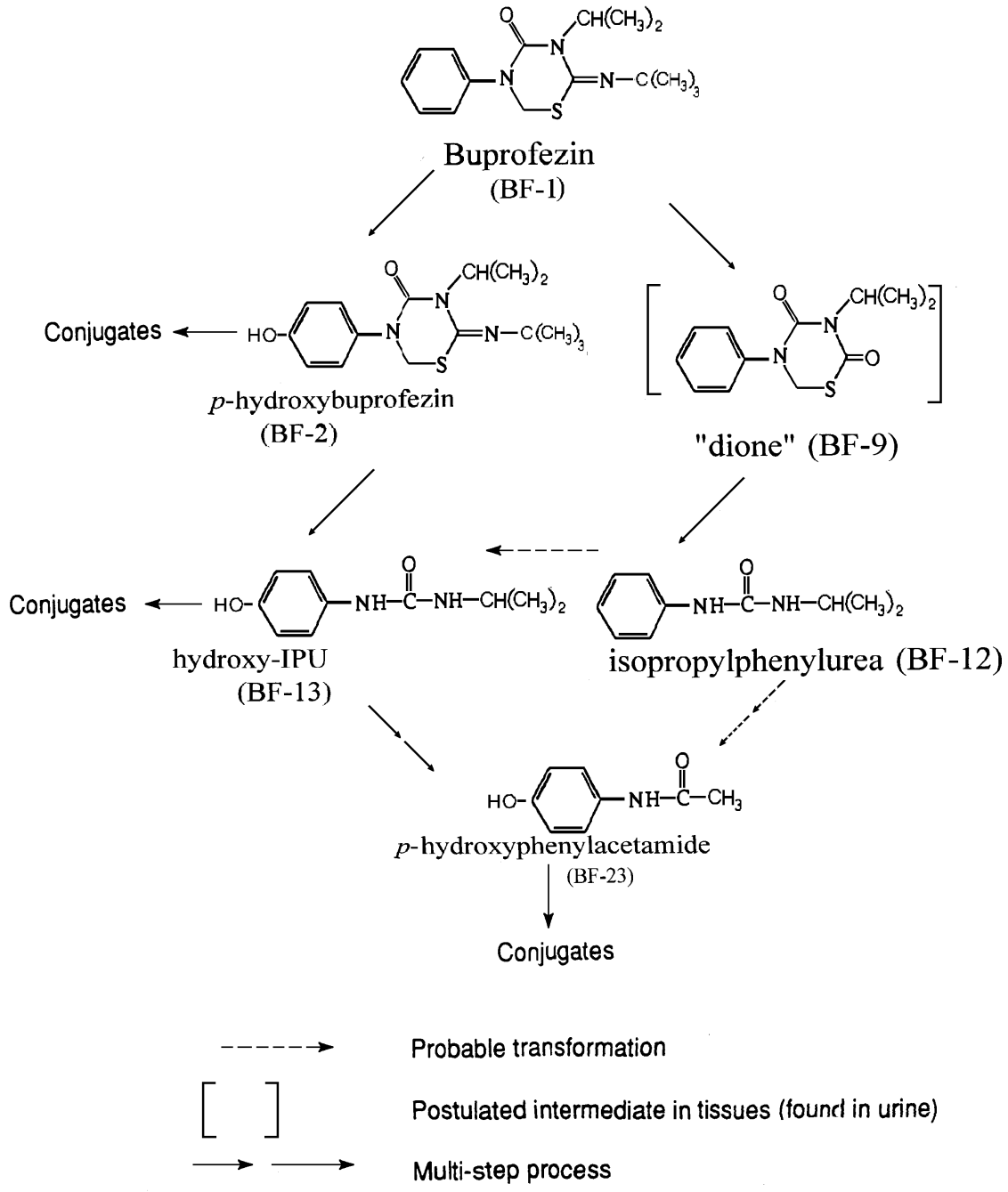
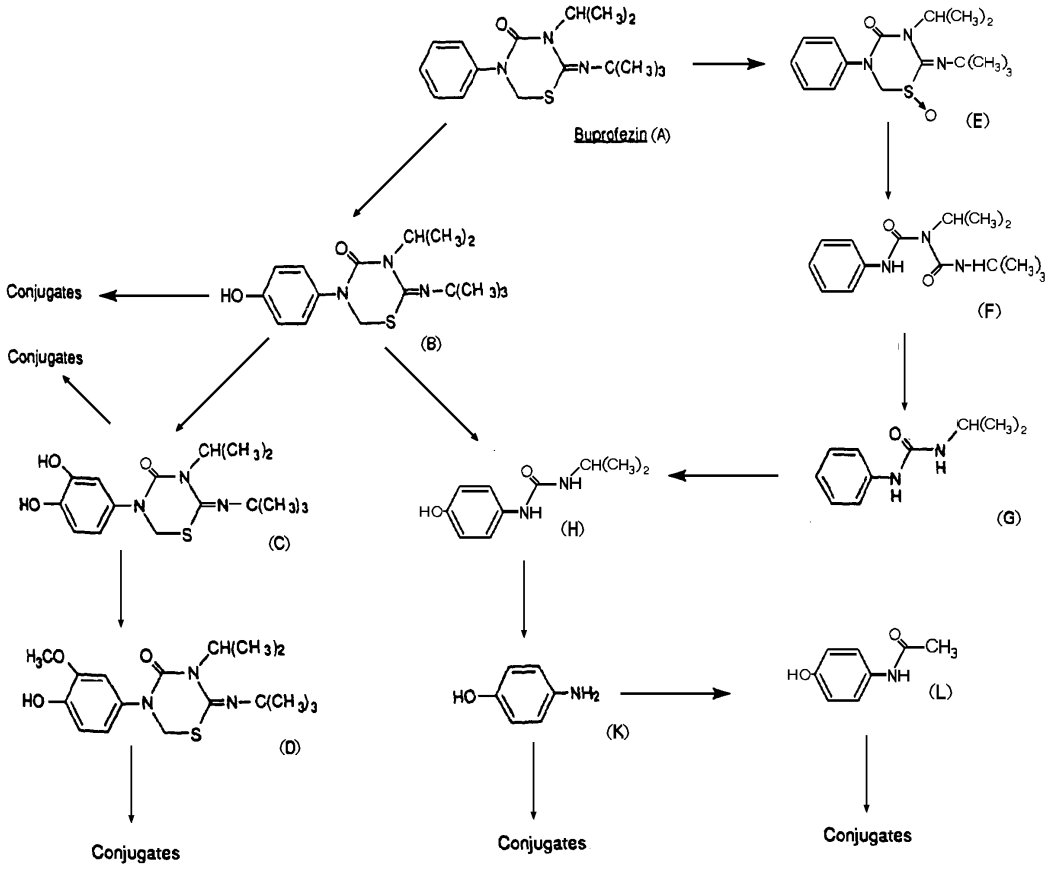


Figure 2. Proposed metabolic pathways of buprofezin in animals.
[1] Shown as J in Fig. 3 of 1991 monograph

Figure 2. Proposed metabolic pathways of buprofezin in animals.



Plant metabolism

The 1991 JMPR reviewed information on the metabolism in plants. More than 90% of the residue 7 days after application to tomato fruits was unchanged buprofezin. In geoponic- or hydroponically-grown rice plants residues were taken up by the roots and translocated to other plant parts, the major residues being unchanged buprofezin and *p*-hydroxybuprofezin. In several other hydroponically-grown plants buprofezin was again the main residue, but the major metabolite was buprofezin sulfoxide. Because of these differences the 1991 Meeting concluded that a study of metabolism in a crop representing a major use was needed and required information on the fate in citrus fruits.

A study of citrus metabolism was completed, reportedly in compliance with US GLP requirements (Rieser and Smith, 1995). [*Phenyl*-^{14}C]buprofezin in an SC formulation was applied to different lemon trees, grown in pots in a glasshouse, according to three regimens. In the first, two applications were made at the equivalent rate of 1 kg ai/ha and 50 g ai/hl, the first 75 days and the second 14 days before harvest in accordance with the "normal" GAP. The rate and the 14-day PHI are consistent with most GAP reported to the 1991 JMPR.

The actual application was to fruit approaching maturity with a micropipette in approximately 200 ì l (0.46 mg ai/ml = 0.05%) estimated to simulate applications to run-off. In the second regimen only the first 75-day treatment was applied, and in the third the treatment was at 3.5 kg ai/ha 30 days before

harvest in order to facilitate the identification of metabolites.

The potential for residue translocation was investigated by application at an equivalent of 2 kg ai/ha to the twigs and leaves of greenhouse trees with immature fruit, with harvest after 28 days. The proportions of the ^{14}C translocated to immature fruit were 0.6-1.2% (0.005-0.006 mg/kg buprofezin equivalents) from twigs and 0.07-0.12% (0.002-009 mg/kg) from leaves.

For the metabolism part of the study, surface residues were removed by washing with ethanol. The washed fruits were separated into peel and pulp which were separately extracted with successively more polar solvents (acetonitrile, 1:1 acetonitrile/water and (by Soxhlet) water). These extracts were combined and extracted with ethyl acetate without adjustment of pH and at pH 2 and pH 10. The ethyl acetate extracts and the remaining fibre containing >10% of the residue (or >0.05 mg/kg) were hydrolyzed with HC1 in dioxane. The hydrolysates were again extracted with ethyl acetate (pH unadjusted, pH 7 and pH 10). Fractions were analysed by one- or two-dimensional TLC and HPLC. The identity of metabolite A was also confirmed by tandem MS (HPLC-MS-MS). The total radioactivity in individual fractions was determined by combustion analysis and scintillation counting.

On day 0 essentially all of the radioactivity was in or on the peel and 93-97% was in the surface wash. The distribution of radioactivity after other intervals is shown in Table 3.

Table 3. Radioactivity in lemons treated with buprofezin labelled in the phenyl ring (Rieser and Smith, 1995).

Treatment		PHI (days)	Mean residue, mg/kg buprofezin equiv. or % of total ^{14}C						
			Total (mg/kg)	Surface wash mg/kg (% of total)	Peel		Pulp		Recov., % of applied
No.	Rate (kg ai/ha)				Extractable mg/kg (% of total)	Non-extractable mg/kg (% of total)	Extractable mg/kg (% of total)	Non-extractable mg/kg (% of total)	
1	1	75	0.4	0.06 (15.8)	0.3 (74)	0.04 (8.9)	0.006 (1.2)	<0.001 (0.1)	41.8
2	1	14	0.9	0.6 (65)	0.3 (31.8)	0.03 (2.8)	0.003 (0.3)	<0.001 (<0.1)	65
1	3	30	3.8	3.0 (78.7)	0.7 (19.2)	0.06 (1.6)	0.02 (0.5)	0.001 (<0.1)	95

The distribution of the compounds identified in extracts from the lemons treated once at 1 kg ai/ha (75-day PHI) is shown in Table 4 and that from those treated twice (14-day PHI) in Table 5.

Table 4. Residues in glasshouse-grown lemons from a single treatment with buprofezin at 1 kg ai/ha after a 75-day PHI (Rieser and Smith, 1995).

Sample	Buprofezin % of TRR (mg/kg)	"Dione", BF-9 % of TRR (mg/kg)	IPU, BF-12 % of TRR (mg/kg)	Metabolite A[1] % of TRR (mg/kg)	Metabolite B[2] % of TRR (mg/kg)	Remainder[3] % of TRR (mg/kg)
Peel						
Wash	13.9 (0.06)	--	--	--	--	0.4 (0.001)
Organic hydrolysis, organic extract	2.9 (0.012)	3.4 (0.014)	2 (0.008)	1.5 (0.006)	1.0 0.004)	2.1 (0.008)
Organic hydrolysis, aqueous extract	NA[4]	NA	NA	NA	NA	<0.1 (<0.001)

Sample	Buprofezin % of TRR (mg/kg)	"Dione", BF-9 % of TRR (mg/kg)	IPU, BF-12 % of TRR (mg/kg)	Metabolite A[1] % of TRR (mg/kg)	Metabolite B[2] % of TRR (mg/kg)	Remainder[3] % of TRR (mg/kg)
Aqueous hydrolysis, organic extract	0.8 (0.003)	3.2 (0.013)	4.5 (0.018)	31.3 (0.126)	6.9 (0.028)	7.3 (0.03)
Aqueous hydrolysis, aqueous extract	NA	NA	NA	NA	NA	6.2 (0.025)
Fibre hydrolysis, organic extract	0.8 (0.003)	0.7 (0.003)	1.6 (0.006)	1.2 (0.005)	1.2 (0.005)	1.5 (0.006)
Fibre hydrolysis, aqueous extract	NA	NA	NA	NA	NA	1.8 (0.007)
Hydrolysd fibre	NA	NA	NA	NA	NA	1.9 (0.008)
Pulp						
Pulp	NA	NA	NA	NA	NA	2 (0.012)
Totals	18.4 (0.08)	7.3 (0.03)	8.1 (0.03)	34 (0.14)	9.2 (0.04)	23.2 0.10

[1] Metabolite A = 2-amino-2-methylpropyl 2-isopropyl-4-phenylallophanate (see (Q), Figure 3, for structure)
[2] Unidentified
[3] No single unidentified peak was greater than metabolite B
[4] NA = not analysed

Table 5. Residues in lemons from two treatments of glasshouse-grown trees with buprofezin at 1 kg ai/ha with a 14-day PHI (Rieser and Smith, 1995).

Sample	Buprofezin % of TRR (mg/kg)	"Dione" % of TRR (mg/kg)	IPU % of TRR (mg/kg)	Metabolite A[1] % of TRR (mg/kg)	Metabolite B[2] % of TRR (mg/kg)	Remainder[3] % of TRR (mg/kg)
Peel						
Wash	63.8 (0.533)	--	--	--	--	0.4 (0.004)
Organic hydrolysis, organic extract	2.0 (0.016)	5.2 (0.043)	0.5 (0.004)	0.8 (0.007)	1.3 (0.011)	2.4 (0.022)
Organic hydrolysis, aqueous extract	NA[4]	NA	NA	NA	NA	0.2 (0.002)
Aqueous Hydrolysis, organic extract	0.2 (0.002)	0.8 (0.006)	1.2 (0.010)	4.9 (0.041)	2.3 (0.019)	4.7 (0.039)
Aqueous hydrolysis, aqueous extract	NA	NA	NA	NA	NA	6.9 (0.058)
Fibre	NA	NA	NA	NA	NA	2.2 (0.018)
Pulp						
Pulp	NA	NA	NA	NA	NA	0.3 (0.003)
Totals	66 (0.55)	6 (0.05)	1.7 (0.014)	5.7 (0.05)	3.6 (0.03)	17.1 (0.15)

[1] Metabolite A = 2-amino-2-methylpropyl 2-isopropyl-4-phenylallophanate (see (Q), Figure 3, for structure)
[2] Unidentified
[3] No single unidentified peak was greater than metabolite B
[4] NA = not analysed

Separate aliquots of unhydrolysed aqueous fractions from the lemons treated once at 1 kg ai/ha (75-day PHI) were also incubated with ß-glucuronidase, ß-glucosidase or cellulase. The proportions of the radioactivity released were 34.1%, 16.6% and 21.1% respectively. Most of this was associated with unresolved polar fractions, and all three incubation systems contained small amounts of the dione metabolite and moreof the allophanate (metabolite A) and IPU.

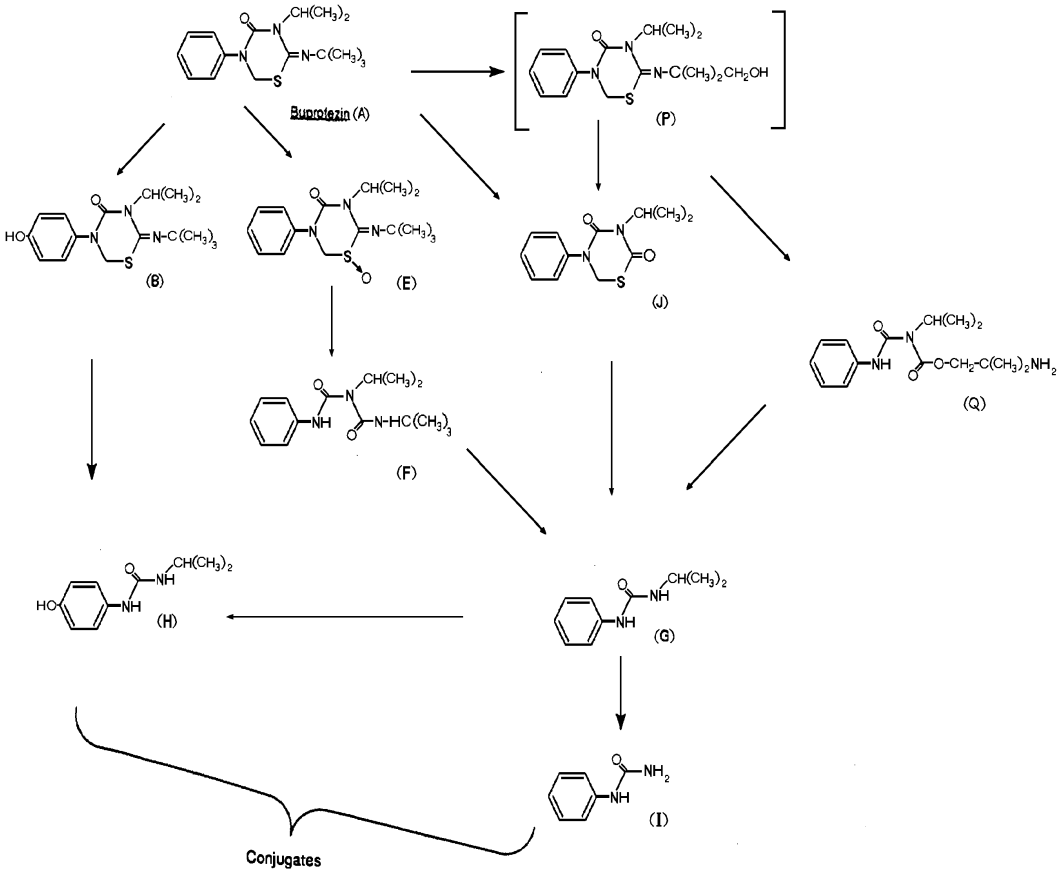
In the translocation experiment ≤1.2% of the radioactivity applied the stems and <2% of that applied to the leaves was translocated into immature fruit.

The manufacturer reported that there was no evidence of the thiobiuret (O, BF-25) in the citrus metabolism study, nor of buprofezin sulfoxide (E, BF-10) or 1-*tert*-butyl-3-isopropyl-5-phenylbiuret (F, BF-11) (Nokata, 1995).

Previous work had shown that a compound with similar chromatographic properties to metabolite A is formed by the acid degradation of BF-4. The preparation and purification of this product from the large-scale degradation of BF-4 allowed the structure of metabolite A to be confirmed by MS. Compound BF-4 was postulated to be an intermediate metabolite in citrus, although it was not actually detected.

On the basis of these findings the authors proposed the metabolic pathway for plants shown in Figure 3.

Figure 3. Proposed metabolic pathways of buprofezin in plants



B = BF-2 2-*tert*-butylimino-5-(4-hydroxyphenyl)-3-isopropyl-1,3,5-thiadiazinan-4-one
E = BF-10 2-*tert*-butylimino-3-isopropyl-5-phenyl-1,3,5-thiadiazinan-4-one 1-oxide
F = BF-11 1-*tert*-butyl-3-isopropyl-5-phenylbiuret
G = BF-12 1-isopropyl-3-phenylurea
H = BF-13 1-(4-hydroxyphenyl)-3-isopropylurea
I = BF-16 phenylurea
J = BF-9 3-isopropyl-5-phenyl-1,3,5-thiadiazinane-2,4-dione
P = BF-4 tetrahydro-2-[(2-hydroxy-1,1-dimethylethyl)imino]-3-isopropyl-5-phenyl-1,3,5-thiadiazin-4-one (hydroxy-*tert*-butyl-buprofezin)
Q = metabolite A 2-amino-2-methylpropyl 2-isopropyl-4-phenylallophanate

Environmental fate in soil and water/sediment systems

Hydrolysis in water

The 1991 JMPR reviewed a hydrolysis study conducted in the dark at pH 4 in which the major degradation product (41.7%) after 11 days was reported as 1-*tert*-butyl-3-isopropyl-5-phenyl-2-thiobiuret (hereafter referred to as "the thiobiuret") Buprofezin (55%) and 1-isopropyl-3-phenylurea (IPU, 14.7%) were also reported. Evidence suggested to the Meeting that IPU resulted from degradation of the thiobiuret under the acidic conditions. The thiobiuret was also reported at much lower levels from the exposure of buprofezin in sterile dionized water to natural sunlight.

Since biological systems may be substantially acidic the 1991 Meeting questioned why the thiobiuret was not reported in the submitted metabolism studies, to which the manufacturer responded that radiograms from these studies "did not show evidence of this compound". Because the studies did not provide proof of the identity of the thiobiuret the 1991 JMPR required such proof, and requested that samples from any future metabolism studies or field trials should be analysed for this compound if it was shown to have occurred at significant levels.

In response to the 1991 requirements the Meeting received confirmation of the identity of the thiobiuret formed during hydrolysis under acidic conditions (Kimura and Nishizawa, 1994) and comments on its relevance to residue levels (Nokata, 1995). In the 1994 confirmatory hydrolysis study buprofezin was stored for 6 days in the dark in water buffered at pH 5 at 45°C, as compared with the incubation for 11 days at pH 4 and 35°C in the study reviewed by the 1991 JMPR.

The thiobiuret was isolated from the hydrosylate by silica gel chromatography and further purified by gel permeation chromatography. The hydrosylate was reported to contain unchanged buprofezin, the thiobiuret and IPU, although the report did not list the relative amounts. 41.4 mg of the purified thiobiuret was obtained from the initial 480 mg of buprofezin, which suggests that about 9% of the buprofezin was degraded to the thiobiuret under these conditions. The purified degradation product was subjected to MS and NMR analyses. MS indicated a molecular weight of 293, as required for the thiobiuret. NMR indicated the loss of the methylene protons in the thiadiazine ring and the appearance of an amino proton, both of which indicate cleavage of the ring. This, together with the appearance of a thiocarbonyl carbon (C=S) in the degradation product, the mass spectrum and other observations, confirmed the identity of the compound as the thiobiuret.

The comments by Nokata (1995) cite the absence of the thiobiuret as a metabolite in the citrus metabolism study as evidence that there is no need to regulate this compound in plants.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The analytical method PPRAM 82, which had been used for most of the residue trials reviewed by the 1991 JMPR, was received too late for review at that Meeting and lacked validation for fruiting vegetables. The 1991 JMPR required validations of the method. Several studies relevant to the analysis of buprofezin or its metabolites were provided.

The first describes a clean up procedure for the determination of buprofezin and *p*-hydroxybuprofezin in crops (Nishizawa *et al.*, 1994). Samples are extracted with acetone or methanol, partitioned between hexane and 1N HCl, neutralized and extracted with hexane for determination by GLC with an AFID. Hydroxybuprofezin is acetylated with acetic anhydride before analysis. Reported "limits of detection" were 0.005 mg/kg in hulled rice, citrus pulp and tomato and 0.01 mg/kg in rice straw and citrus peel. Reported recoveries were 75-97% at 0.1 or 0.2 mg/kg fortification levels.

The few published chromatograms from hulled rice and tomato samples suggest that reasonable limits of determination would be 0.01 and 0.02 mg/kg for buprofezin and *p*-hydroxybuprofezin respectively in hulled rice and 0.02 mg/kg for both in tomatoes. However, the method was not validated below 0.1 mg/kg. Chromatograms from citrus were not included. The extraction of buprofezin from

hulled rice by acetone or methanol was shown to be acceptable.

In the second study, three methods were assessed for the extraction of buprofezin residues from peppers, beans and egg plants (García *et al.*, 1993). In the first (Mills *et al.*, 1963) the chopped sample is extracted with acetonitrile and partitioned into hexane after diluting with water. In the second (Luke *et al.*, 1975, 1981) samples are extracted with acetone and partitioned with petroleum ether and methylene chloride. In the third (Leary, 1971) extraction is with ethyl acetate, with clean-up on a short Florisil column. Recoveries of buprofezin were >81% for all three extraction procedures at 0.1 mg/kg fortification levels from each of the crops tested, but were better with the Leary extraction (>89% in all crops at 0.1 mg/kg). The Leary extraction was also tested at 0.02 mg/kg fortification levels and gave >93% recoveries from all the crops.

Another procedure is based on extraction with acetone, concentration to an aqueous solution, partitioning into dichloromethane under basic conditions and determination of buprofezin by GLC with a nitrogen detector (Dick and Rounds, 1984). This appears to be the method used to produce most of the data provided to the 1991 JMPR (except in the Japanese trials) and referred to in the 1991 monograph as ICI method PPRAM 82. The reported limit of determination was 0.005 to 0.01 mg/kg. The only reported recoveries were 101% at 0.1 mg/kg and 95% at 0.5 mg/kg fortification levels. The few chromatograms provided suggest that residues may be quantified at 0.01 mg/kg in tomatoes, although the only two controls were reported as <0.01 and 0.6 mg/kg.

A study of the extractability of weathered buprofezin residues from peaches by various solvent systems (Roberts-McIntosh, 1991) was supplied in response to the 1991 JMPR requirement for validation of analytical method PPRAM 82. A sample of peaches which had been treated with buprofezin at 60 g ai/ha and harvested after 7 days "and analysed in June 1990 (ref. 3) using ICI Plant Protection Division Analytical Method (PPRAM) 82 was found to contain a residue of 0.66 mg/kg". The peaches were stored at -20°C until selected for the study in 1991. Five extraction systems were investigated and the results of analyses by PPRAM 82 are summarized in Table 6. The "ref. 3" quoted was not provided to the present Meeting.

Table 6. Extractability of buprofezin in weathered peaches harvested 7 days after treatment at 60 g ai/ha (Roberts-McIntosh, 1991).

Extraction method	Mean residue[1] (mg/kg)		% Recovery[2]
	Treated	Control	
Cold acetone	0.65	ND[3]	83
Cold methanol/water (90:10)	0.68	ND	87
Cold acetone/hexane (80:20)	0.78	ND	86
Acetone reflux	0.67	ND	68
Methanol/water reflux (90:10)	0.52	ND	80
Mean	0.66	--	80.1

[1] Mean of 3 assays, uncorrected for recovery
[2] From 0.5 mg/kg fortification
[3] ND = not detected (<0.005 mg/kg)

Summary recovery data for cucumbers and gherkins (74-106%) and tomatoes (79-91%) were also provided to the Meeting (Olthof, 1995). Although the LOD was reported to be 0.01 or 0.02 mg/kg for each vegetable, no fortification levels, controls or chromatograms were provided.

A recent analytical method (RAM No. BF/06/94) has been described for the determination of buprofezin, BF-12 (1-isopropyl-3-phenylurea) and BF-9 (the "dione" or 3-isopropyl-5-phenyl-1,3,5-

thiadiazinane-2,4-dione) in tomatoes (Neal, 1994). The metabolites had been identified in lettuce. Samples are extracted with acetone, the acetone is evaporated and the aqueous remainder acidified. BF-9 is extracted with hexane, the aqueous solution is neutralized and buprofezin and BF-12 are extracted with ethyl acetate/hexane. The BF-9 fraction is cleaned up on a Florisil column, all the extracts are combined and concentrated, and the three compounds are determined by GLC with an NPD.

During development of the method recoveries were 94% for buprofezin and 79 and 91% for BF-12 and BF-9 respectively at 0.01 mg/kg, reported to be the limit of determination. The lowest validated levels in the processing study were 0.05 mg/kg. Mean buprofezin recoveries at this level were fruit 86%, wet pomace 80%, dry pomace 79%, juice 108%, purée 101 % and paste 123%, with similar recoveries of the metabolites. A limit of determination of 0.05 mg/kg for each compound in each tomato product is reasonable.

Other analytical methods for buprofezin or *p*-hydroxybuprofezin are described in the 1991 monograph.

Stability of pesticide residues in stored analytical samples

Information already reviewed by the 1991 JMPR (Bioanalytical Research, 1991) was re-submitted. From this study the 1991 JMPR reported no significant loss of buprofezin from apples, peaches or courgettes and only 13% from kiwifruit after storage up to a year at -20°C. Information on the stability of buprofezin and *p*-hydroxybuprofezin in stored analytical samples of citrus (Iwamoto and Matano, 1993) and buprofezin in cucumbers (Iwamoto and Nishizawa, 1993) and tomatoes (Iwamoto and Kanauchi, 1994) was provided to the present Meeting and is discussed later under "Residues resulting from supervised trials".

Mean recoveries of 80-106% of both buprofezin and *p*-hydroxybuprofezin were attained after storage of citrus pulp for 56-58 days and citrus peel for 91-93 days at -20°C when fortified at 0.5 mg/kg.

In cucumbers fortified at 0.2 mg/kg, 90% of the residue was reported to remain after 130 days at -20°.

Mean recoveries from tomatoes fortified at 0.05 mg/kg and stored at four sites for periods of 53-94 days ranged from 100 to 114%.

Residue definition

On the basis of a tomato metabolism study indicating that over 90% of the residue in tomatoes is unchanged buprofezin the 1991 JMPR defined the residue as buprofezin. That Meeting also required additional information on the fate of residues in animals, water, and citrus, which were supplied and are described above.

The citrus metabolism study confirms unchanged buprofezin to be the main residue (66% of the total ^{14}C) after 14 days and the second most abundant (18%) even after 75 days. After 75 days the main residue was (Q) or metabolite A (2-amino-2-methylpropyl 2-isopropyl-4-phenylallophanate). No significant residues of buprofezin sulfoxide (reported in hydroponic metabolism studies) or the

phenylbiuret metabolite were reported, nor was there any evidence of the thiobiuret known to be formed under acidic conditions in water. In the data on supervised trials submitted to the Meeting no residues of *p*-hydroxybuprofezin were reported in citrus or tomatoes.

These findings support the 1991 JMPR's conclusion that buprofezin *per se* is the appropriate definition of the residue, at least for regulatory purposes for cucumbers, tomatoes and oranges. This definition may need to be re-assessed if MRLs are recommended in the future for additional crops, since metabolism varies among plants of different types.

As discussed in the appraisal, the definition of the residue in animal products will have to be determined if it is decided in the future that limits are needed for them.

USE PATTERN

Information on approved uses of buprofezin provided to the Meeting is summarized in Table 7.

Table 7. Approved uses of buprofezin on crops.

Crop, country	Application				PHI, days	Notes
	Form.	kg ai/ha	kg ai/hl	No.		
Citrus fruits						
Spain[1]	WP?	0.4-1	0.01-0.025	1	7	
New Zealand	WP	0.375	0.0125	2-6	14	high vol. to run-off
Cucumbers						
Germany	SC	0.5-0.9	0.0075	1	--	At infestation
Netherlands	EC	0.04-0.11	0.007	2	3	Glasshouse
UK	SC	0.075-0.375	0.0075	8*	3	Glasshouse. * max. 2 treatments, 45 day interval
Egg plants						
UK	SC	0.075-0.375	0.0075	2	3	Glasshouse
Grapes (wine and table)						
New Zealand	WP	0.125	0.0125	2	*	*pre-flower, high vol. to run-off
Gherkins						
Netherlands	EC	0.04-0.11 (0.05-0.08)*	0.007	2	3	Glasshouse *Field use
Kiwifruit						
New Zealand	WP	0.25	0.0125	1-2	*	*pre-flower, high vol. to run-off
Melons						
Netherlands	EC	0.04-0.11	0.007	2	3	Glasshouse
Persimmons						
New Zealand	WP	0.25	0.0125	2	*	*pre-flower, high vol. to run-off
Peppers (sweet)						
Germany ("peppers")	SC	0.5-0.9	0.0075	1	--	at infestation
Netherlands	EC	0.04-0.11	0.007	2	3	Glasshouse
UK	SC	0.075-0.375	0.0075	2	3	Glasshouse
Pome fruit						
New Zealand	WP	0.375 (pear to 0.625)	0.0125	2	*	*pre-flower, high vol. to run-off

Crop, country	Application				PHI, days	Notes
	Form.	kg ai/ha	kg ai/hl	No.		
Summer squash						
Netherlands	EC	0.04-0.11 (0.05-0.08)*	0.007	2	3	Glasshouse *Field use
Tamarillos						
New Zealand	WP	0.275	0.0125	2	7	high vol. to run-off
Tomatoes						
Germany	SC	0.5-0.9	0.0075	1	--	at infestation
Netherlands	EC	0.04-0.11	0.007	2	3	Glasshouse
UK	SC	0.075-0.375	0.0075	8	3	Glasshouse. 2 treatments max. in 65-day period

[1] Application rate not supported by label, but reported in manufacturer's working paper. Number of applications from 1991 JMPR monograph.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The 1991 JMPR required additional data on outdoor supervised trials on cucumbers and tomatoes if outdoor uses were shown to be GAP, and additional data on supervised trials on oranges, including the final report on the Brazilian trials on which only a draft report had been provided. For the additional trials the 1991 Meeting required analyses for *p*-hydroxybuprofezin (the main metabolite in geoponic and hydroponic metabolism studies on rice), the thiobiuret derivative (formed by hydrolysis under acidic conditions), buprofezin sulfoxide and the phenylbiuret metabolite (the major metabolites in hydroponic studies on several crops). Unchanged buprofezin had been the only significant residue found in a study of tomato metabolism. Data were provided on residue trials on cucumbers, tomatoes and citrus.

No MRLs were recommended by the 1991 JMPR for animal products. Although that Meeting reviewed a conventional dairy cow feeding study, no study of ruminant metabolism had been provided. The 1991 Meeting drew tentative conclusions, but recommended reconsideration when the required studies on the fate of residues during processing and on animal metabolism had been reviewed . These studies were provided to the present Meeting.

Plants

Citrus. The 1991 JMPR recommended a TMRL of 0.3 mg/kg for oranges, based trials in Japan, South Africa and Portugal, but mainly Japan because the others did not closely reflect maximum GAP conditions. The present Meeting received data on natsudaidais from Japan and on oranges from Spain and Brazil, the last being the final report required by the 1991 JMPR. The results are shown in Table 8.

In the Brazilian trials 3 knapsack mistblower applications were made to "Pera Natal" orange trees in 1000 m^2 plots (within a 5000 m^2 grove). The trials were conducted according to FAO guidelines. Samples were received at the laboratory within 6 hours of harvest and stored at -15°C until analysis (<2 weeks). Analyses were by the method of Nihon Nohyaku (1985) described in the 1991 evaluation. The limit of "detection" was reported as 0.01 mg/kg, although the chromatograms provided were not sufficiently legible for an independent assessment of a limit of determination. Reported recoveries (not documented) from peel, juice and bagasse fortified at 0.1 mg/kg were 85-95%. The results were provided uncorrected, but are shown corrected for recoveries in Table 8.

The Spanish trials (3 locations, 128-200 m^2 plots) were reported to be conducted according to OECD GLP. The report was well documented. Samples were frozen shortly after harvest and stored at -20°C until analysis (approximately 80 days after field sampling) by HPLC for both buprofezin and *p*-

hydroxybuprofezin (separate peaks). Extraction was with acetone and clean-up by successive hexane partitions under acidic and neutral conditions (similar to Nishizawa *et al.*, 1994). Recoveries of buprofezin and *p*-hydroxybuprofezin from whole oranges were about 90-100% and 75-84% respectively at 0.02 and 0.5 mg/kg fortification levels. No residues (<0.015 mg/kg) of the metabolite were found in any sample. Representative chromatograms suggest that a limit of determination of 0.02 mg/kg is possible for both compounds in whole oranges.

In the Japanese 2-tree plot trial buprofezin (WP) was applied by knapsack sprayer at 25g ai/hl and 5000 l/ha (25 g ai/hl, with a 14-day PHI, is confirmed GAP). Samples were sent to the laboratory "shortly after harvest" for analysis for buprofezin and *p*-hydroxybuprofezin. They were stored at -10°C until analysis, although the handling and storage conditions before receipt at the laboratory and the interval from field sampling to analysis were not stated. The report was completed in December 1993. Mean recoveries of both compounds at fortification levels of 0.5 mg/kg were 80-106% after storage of pulp for 56-58 days and peel for 91-93 days at -20°C. Although the sampling-to-analysis intervals for the field-treated samples were not stated, the storage stability study was completed in April-July 1988.

Samples for analysis were extracted with acetone. The extract was adjusted to pH 7-8, extracted with hexane and partitioned with acetonitrile. The last extract was concentrated and cleaned up on a silica gel column, which was also used to separate the parent compound from the metabolite, and both compounds were determined by GLC with an NPD. Recoveries of 91 and 100% were reported for buprofezin and *p*-hydroxybuprofezin respectively at 0.1 mg/kg fortification levels. The limit of determination was reported as 0.01 mg/kg, although chromatograms suggest that 0.02-0.05 mg/kg might be more realistic for routine analyses, especially since recoveries were only verified at 0.1 mg/kg. All controls were reported as <0.01 mg/kg for both compounds.

Table 8. Buprofezin residues in citrus fruit resulting from supervised trials. Underlined residues are from treatments according to GAP.

Country, year	Application/treatment			Sample	Residues (mg/kg) at PHI (days)						Ref.
	Form.	No.	kg ai/ha (kg ai/hl)		7	28	63	91	105		
Oranges											
Brazil 1990	25% WP	3	0.5 (0.03)	Peel		0.2 0.1	0.10 0.19	0.03 0.01	0.02 0.01		1
				Juice		<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01		
				Finisher pulp		<0.01 <0.01	<0.01 <0.01	<0.01 <0.01	<0.01 <0.01		
				Whole fruit[1]		0.04 0.02	0.02 0.04	<0.01 <0.01	<0.01 <0.01		
Spain 1994	25% WP	1	1 (0.025)	Peel	<u>0.05</u>						2
				Pulp	<u>0.02</u>						
				Whole fruit	<u>0.06</u>[2]						
	25% WP	1	1 (0.025)	Peel	<u>0.07</u>						
				Pulp	<u><0.02</u>						
				Whole fruit	<u>0.03</u>[2]						
	25% WP	1	1 (0.025)	Peel	<u>0.11</u>						
				Pulp	<u><0.02</u>						
				Whole fruit	<u>0.03</u>[2]						

Country, year	Application/treatment			Sample	Residues (mg/kg) at PHI (days)						Ref.
	Form.	No.	kg ai/ha (kg ai/hl)		7	28	63	91	105		
Natsudaidais											
Japan 1987-88	25% WP	5	1.25 (0.025)	Peel	Residue (mg/kg) at PHI (days)						3
					21	30	45	90	120	150	
					1.9 1.7	1.2 1.1	0.7 0.6	0.4 0.4	0.5 0.5	0.2 0.2	
				Pulp	0.3 0.3	0.2 0.2	0.07 0.07	0.03 0.03	0.02 0.02	0.01 0.01	
				Whole fruit[3]	0.7	0.4	0.2	0.2	0.2	0.08	

[1] Residues in whole fruit estimated on basis of 20.3% peel weight. All results corrected for recoveries. Duplicate results are from separate plots.
[2] *p*-hydroxybuprofezin was not detected (<0.015 mg/kg) in pulp, peel or whole oranges. All results are means of duplicate injections. Residues in whole fruit are from analyses of whole oranges.
[3] *p*-hydroxybuprofezin was not detected (<0.005 mg/kg) in pulp, peel or whole fruit. Residues in whole fruit estimated on basis of pulp/peel weight ratio of 2.2:1.

References

1. Salgado, 1990
2. Melkebeke and Genijen, 1995a
3. Iwamoto and Matano, 1993

Cucumbers. The temporary MRL of 0.3 mg/kg recommended by the 1991 JMPR was based on data (mainly from indoor trials) from The Netherlands, the UK, Greece and Japan. Maximum residues representing GAP were 0.06 mg/kg from The Netherlands (3-day PHI) and Greece (7-day PHI) and 0.21 mg/kg from proposed UK GAP (3-day PHI). The highest residues from trials according to GAP in a Japanese trial were 0.13 mg/kg after three days (the GAP PHI is 1 day), but at only 0.6 times the maximum permitted rate. Residues were 0.6 mg/kg at 1 day from twice the maximum GAP rate. Because only the trials in Greece were outdoor the 1991 Meeting required additional data from outdoor trials if outdoor uses were confirmed to be GAP.

All GAP for buprofezin uses on cucumbers reported to the present Meeting (see Table 7) were for glasshouse treatments, although GAP for gherkins in The Netherlands also included field uses. Current GAP in The Netherlands and the UK (now authorized) essentially confirms that reported in 1991. GAP was also reported for German glasshouse uses, in which the rate of 0.0075 kg ai/hl is essentially the same as in The Netherlands and the UK

Additional data were received from Japanese supervised trials with 3 applications at 0.025 kg ai/hl (0.6-0.75 kg ai/ha) and PHIs of 1, 3 and 7 days.

The application rates in terms of kg ai/ha were in accordance with Japanese GAP reported in the 1991 monograph, as was the 1-day PHI. Trials were conducted at 4 sites, in which the plots were 14-22 m^2 and application was by knapsack power sprayer. Samples were sent to the test facility "just after harvest" where they were stored at -20°C until analysis for buprofezin (only) ≤1 month after field sampling.

Analysis was by the method of Nishizawa *et al*. (1994), with 98% recoveries from samples fortified at 0.2 mg/kg. The reported limit of determination was 0.01 mg/kg. Chromatograms of treated samples containing 0.05 mg/kg and controls suggest that this is an achievable level, although it was not validated below 0.2 mg/kg. When samples fortified at 0.2 mg/kg were stored for 130 days at -20°C, the recovery was reported to be 90%.

The results are shown in Table 9.

Table 9. Buprofezin residues in greenhouse-grown cucumbers resulting from supervised trials in Japan in 1992 with a 25% WP Formulation (Iwamoto and Nishizawa, 1993). Underlined residues are from treatments at GAP application rates in terms of ai/ha.

Application			Site	PHI, days	Residues, mg/kg
No.	kg ai/ha	kg ai/hl			
3	0.55-0.75	0.025	1	1	0.8, 0.7
				3	0.25, 0.25
				7	0.09, 0.08
3	0.75	0.025	2	1	0.8, 0.6

Application			Site	PHI, days	Residues, mg/kg
No.	kg ai/ha	kg ai/hl			
			3		0.4, 0.4
			4		0.4, 0.4
			2	3	0.3, 0.3
			3		0.2, 0.2
			4		0.1, 0.09
			2	7	0.09, 0.09
			3		0.09, 0.09
			4		0.05, 0.05

Tomatoes. The temporary MRL of 0.5 mg/kg estimated by the 1991 JMPR was based on trials in The Netherlands, the UK, Greece and Japan, with maximum residues from treatments according to GAP of 0.2 mg/kg in The Netherlands (0.3 mg/kg from 1.3 times GAP rate; GAP is 0.0075 kg ai/hl, 3-day PHI); 0.3 mg/kg in the UK (proposed GAP the same as The Netherlands) and 0.4 mg/kg in Japan (GAP 0.19-1 kg ai/ha or 0.0125-0.025 kg ai/hl). As with cucumbers, additional data were required if field uses were confirmed to be GAP.

No GAP for field uses was reported to the present Meeting, but the application rates cited by the 1991 JMPR for The Netherlands and the UK were confirmed to be authorized GAP in both countries and the same spray concentration, 0.0075 kg ai/hl, was reported as GAP in Germany. Additional data were provided from Italy on field trials and from Japan on glasshouse trials.

The Italian outdoor tomato trials were at three locations in Northern Italy, all on 30 m^2 plots and reportedly according to OECD GLP. Samples were stored in an acceptable manner and analyses were within 4 months of sampling. The analytical method was similar to that for cucumbers, but the determination of buprofezin and *p*-hydroxybuprofezin was by HPLC instead of GLC. Mean recoveries were 102% for buprofezin and 106% for *p*-hydroxybuprofezin at 0.02 mg/kg and 86 and 94% respectively at 0.5 mg/kg. Chromatograms from controls and samples spiked at 0.02 mg/kg suggest that an LOD of 0.01 to 0.02 mg/kg is reasonable.

The Japanese glasshouse trials were at four sites, on plots of 5, 8.1, 50 and 90 m^2, with applications by knapsack power sprayer. Samples were stored at -20°C until analysis within approximately 3 months of harvest. The analytical procedure was similar to that for cucumbers, except a partition into dichloromethane preceded addition of the acid for the acidic hexane extraction. Average recoveries were 94% at 0.1 mg/kg and the reported limit of "determination" was 0.005 mg/kg, although this appears to be a limit of detection. Controls ranged from <0.005 to 0.04 mg/kg. Mean recoveries after storage at the four sites for periods of 53-94 days ranged from 100 to 114% at 0.05 mg/kg fortification levels. An LOD of 0.05 mg/kg would appear to be reasonable on the basis of the chromatograms provided. The results are shown in Table 10.

Table 10. Residues of buprofezin in tomatoes resulting from indoor and outdoor supervised trials with WP formulation. Underlined residues are from applications according to GAP.

Country, year	Application			Site[1]	PHI, days	Residues, mg/kg	Ref.
	No.	kg ai/ha	kg ai/hl				
Outdoor field trials (buprofezin and *p*-hydroxybuprofezin)[2]							
Italy 1994	2	0.25	0.025		0	0.10	Melkebeke and Genijen, 1995b

Country, year	Application			Site[1]	PHI, days	Residues, mg/kg	Ref.
	No.	kg ai/ha	kg ai/hl				
				1			
					2	0.08	
					7	0.09	
					14	0.03	
	2	0.25	0.025	2	2	0.08	
	2	0.25	0.025	3	2	0.17 Tomatoes 0.03 Juice 0.15 Purée	
Glasshouse trials (analysis for buprofezin only)							Iwamoto and Kanauchi, 1994
Japan 1993/94	3	0.625	0.025	1	1	0.7, 0.7	
					3	0.6, 0.6	
					7	0.4, 0.4	
	3	0.75	0.025	2	1	0.4, 0.4	
				3		0.3, 0.3	
				4		0.3, 0.3	
				2	3	0.3, 0.3	
				3		0.2, 0.1	
				4		0.3, 0.3	
				2	7	0.2, 0.3	
				3		0.1, 0.1	
				4		0.3, 0.3 Controls <0.005-0.04 mg/kg[3]	

[1] Site 1: Chiba, 50 m^2 plot. Site 2: Fukushima, 90 m^2 plot. Site 3: Iwate, 8.1 m^2 plot. Site 4: Nagano, 5 m^2 plot.
p-hydroxybuprofezin was not detected (<0.015 mg/kg)
[2] High control was at Site 1. 0.186 ng buprofezin/5 mg sample = 0.04 mg/kg. Submission erroneously recorded 0.01 mg/kg.

Animals

Cows. The 28-day feeding study on dairy cows reviewed by the 1991 JMPR included two feeding levels, 20 and 200 ppm in the diet. The 1991 monograph reported as follows.

> No residues of buprofezin (<0.01 mg/kg) were detected in milk from the low-dose cows. In milk from one of the high-dose cows, buprofezin peaked at 0.04 mg/kg after 21 days, declining to <0.01 mg/kg after a 3-day withdrawal period. No residues (<0.01 mg/kg) from either dose were detected in kidney, liver or muscle. Residues were up to 0.14 and 0.2 mg/kg in subcutaneous and peritoneal fat respectively from the high dose, but _0.02 mg/kg in fat from the low dose.

On the basis of these findings and the temporary limits of 0.5 and 0.3 mg/kg recommended for tomatoes and oranges respectively the 1991 Meeting tentatively concluded that residues of buprofezin *per se* were unlikely in the muscle, kidney, liver or milk of cattle, but concluded that reconsideration might be needed when the required information on processing and studies of animal metabolism were reviewed. These have now been provided and are described below under "Fate of residues in storage and processing" and above under "Animal metabolism".

The 7-day metabolism study on a dairy cow (see above) was with the equivalent of 27 ppm in the diet, a level similar to the 20 ppm low-dose feeding study reviewed by the 1991 JMPR. The metabolism study supports the finding in the feeding trial that residues of buprofezin are unlikely to be found in the muscle, offal or milk of cattle at a dietary intake of 20 ppm. However, it also reveals that the main residue in animal products is *p*-hydroxybuprofezin in liver and kidney and *p*-acetamidophenol in milk, not the parent compound determined in the feeding study. At the 27 ppm feeding level *p*-hydroxybuprofezin occurred at 0.13 mg/kg in liver and 0.07 mg/kg in kidney, with lower levels of other metabolites. In milk the highest residue was *p*-acetamidophenol at 0.002 mg/kg. Residues in muscle (≤0.02 mg/kg buprofezin equivalent) could not be identified.

No information on processing has been provided for citrus, but the tomato processing study showed buprofezin concentrations of 23- and 34-fold in wet and dry pomace respectively. If it is assumed that dry tomato pomace is fed to beef cattle at 25% of the diet (or to dairy cattle at 10%) and residues are at the proposed MRL of 1 mg/kg in the tomato fruit a theoretical worse-case dietary intake of buprofezin from the feeding of dry pomace would be 8.5 ppm in beef cattle and 3.4 ppm in dairy cattle. A similar level would be expected from feeding "citrus pulp" (i.e. a commercial process fraction including extractor residue and peel) if a similar concentration of the residue occurs. Concentration in citrus pulp is likely since most of the residue has been shown to be in the peel.

With these gross assumptions it can be estimated from the metabolism study that residues of the main residue (*p*-hydroxybuprofezin or *p*-acetamidophenol) in cattle could occur at approximately 0.04 mg/kg in liver, 0.02 mg/kg in kidney and <0.001 mg/kg in milk. The significance of this is considered below in the Appraisal.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No information was provided.

In processing

The 1991 JMPR required "information on the fate of buprofezin in commodities in processing (e.g. tomato processing into pulp, juice, ketchup or purée and the Brazilian citrus pulp data cited". In a 1994 study conducted in the USA in accordance with US GLP, a 0.15 ha plot of tomatoes was treated four times by a tractor-mounted high-cycle sprayer with a 40 SC formulation at 1 kg ai/ha (2.4 times the proposed rate) and the tomatoes harvested after 7 days. They were subsequently processed into wet pomace, dry pomace, juice, purée and paste, which were analysed for buprofezin and the metabolites BF-12 (1-isopropyl-3-phenylurea) and BF-9 (the "dione" or 3-isopropyl-5-phenyl-1,3,5-thiadiazinane-2,4-dione) (Neal, 1995).

Simulated commercial processing involved washing, crushing, heating to 196°F and screening (0.033" screen) to yield tomato juice and wet pomace. Dry pomace was produced by overnight drying to 99% dry solid in a dehydrator on trays at approximately 147°F. Juice was canned after heating at 240°F for 51 minutes. Purée was prepared from juice by vacuum evaporation to approximately 13% solids. To produce paste, purée was further evaporated to approximately 26% solids.

The analytical method employed and appended to the study (Neal, 1994) is described above under Analytical methods. An LOD of 0.05 mg/kg should be reasonable for the routine analysis of tomato products by this method, although lower levels may be possible. The residues found are shown in Table 11.

Table 11. Residues of buprofezin and metabolites in processed tomato fractions from tomatoes treated with a 40SC formulation at 1 kg ai/ha and harvested after 7 days (Neal, 1995).

Sample	Residues, mg/kg[1]			Buprofezin concentration/ reduction factor[4]
	Buprofezin (control)	BF-9[2] (control)	BF-12[3] (control)	
Unwashed fruit	0.55 (ND)[5]	ND (ND)	ND (ND)	1.0
Wet pomace	12.7 (0.01)	0.02 (ND)	0.06 (ND)	23.1
Dry pomace	18.6 (0.01)	0.04 (0.02)	0.09 (ND)	33.8
Juice	0.05 (ND)	0.01 (0.01)	0.05 (ND)	0.09
Purée	0.35 (ND)	0.0 (ND)	0.02 (ND)	0.6
Paste	0.68 (ND)	ND (0.01)	0.04 (ND)	1.2

[1] Averages of replicates corrected for recoveries of 93% for buprofezin, 95% for BF-9 and 85% for BF-12. All values below 0.05 mg/kg are below the routine limit of determination.
[2] 3-isopropyl-5-phenyl-1,3,5-thiadiazinan-2,4-dione
[3] 1-isopropyl-3-phenylurea
[4] Residue in sample divided by residue in unwashed fruit
[5] Not detected

Residues in the edible portion of food commodities

Data reviewed by the 1991 JMPR indicated that residues in whole citrus fruit are about 3-10 times the level in the pulp. The trials reviewed by the present Meeting show similar ratios of 3-8 (see Table 8). The above processing study on tomatoes shows that residues are lower in juice and purée than in the original fruit, and at about the same level in tomato paste.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided.

NATIONAL MAXIMUM RESIDUE LIMITS

The only MRLs provided that were not recorded by the 1991 JMPR were New Zealand national MRLs for citrus, 0.5 mg/kg and tamarillos, 0.1 mg/kg.

APPRAISAL

Buprofezin was first evaluated by the 1991 JMPR, which estimated an ADI of 0-0.01 mg/kg bw and recommended TMRLs for cucumbers, tomatoes and oranges with 8 required and 4 desirable items of further work or information. Data were provided in response to the 1991 requirements on the fate of residues in water (acidic conditions), metabolism in ruminants and plants, additional supervised trials on citrus, cucumbers and tomatoes, and other items.

Data provided by the manufacturer allowed the Meeting to conclude that the identity of the thiobiuret metabolite formed in water under acidic conditions had been confirmed.

The 1991 JMPR reviewed data on the metabolism of buprofezin in rats and reports of the metabolic products found in the excreta of hens and proposed a tentative metabolic pathway for animals, but required a ruminant metabolism study. Such a study on a lactating Jersey cow fed the equivalent of 27 ppm in the diet of [^{14}C]phenyl-labelled buprofezin for 7 days was reviewed by the Meeting. More than 64% of the total radioactive dose was excreted in the faeces and urine, over twice as much in faeces as in urine. Tissues and milk accounted for 1.2% of the administered dose, the highest proportion in the liver (0.7%), the next highest in muscle (0.2%) and the lowest in the kidneys (0.04%).

Unchanged buprofezin and p-hydroxybuprofezin were the only identified residues found in the faeces, accounting for 61% of the total radioactive residue (TRR). These two, with isopropylphenylurea (IPU), hydroxy-IPU, acetamidophenol and low levels of the dione metabolite were found in urine (35% of the TRR was identified). No unchanged buprofezin was detected in the liver, kidneys, or milk. None of the several metabolites in the muscle and fat could be identified owing to the low levels present ($\leq$0.02 mg/kg buprofezin equivalent).

In liver the predominant residue was *p*-hydroxybuprofezin (11% of the TRR), with lesser amounts of IPU, hydroxy-IPU and *p*-acetamidophenol (19.1% of the TRR was identified). A similar profile of the same metabolites was found in the kidneys (33% of the TRR identified). In milk (15% of the TRR identified) the same compounds were found, but *p*-acetamidophenol was the predominant residue (9.2% of the TRR). Several unidentified metabolites were also observed in each sample, the major one constituting 5.9, 4.5 and 4.9% of the TRR in the liver, kidneys and milk respectively.

From these findings two basic metabolic pathways are proposed for ruminants. The first is hydroxylation at the para position of buprofezin, followed by cleavage of the thiadiazinane ring and loss of the $-CH_2-S-C=N-C(CH_3)_3$ group to leave hydroxy-IPU which is degraded to N-hydroxyphenylacetamide (*p*-acetamidophenol). The second proposed route involves formation of the dione metabolite (found in urine as well as in citrus metabolism) as an intermediate before cleavage of the thiadiazinane ring with loss of $-CH_2-S-C=O$ to form IPU which is hydroxylated and metabolized by multiple steps also to the acetamidophenol. The dione was not reported in the hen study, but was found in the degradation of buprofezin in soil and water.

The metabolic pathway proposed for ruminants is consistent up to a point with that proposed by the 1991 JMPR for animals on the basis of the data on rats and hens. The difference is an additional hydroxylation of the phenyl ring in rats to form dihydroxyphenyl-buprofezin, followed by methylation of one of the hydroxy groups to form hydroxy-methoxy-buprofezin. Neither of these compounds nor the thiobiuret metabolite were among those used as reference standards in the cow metabolism study. It is possible that unidentified metabolites found in the cow study could have included them.

From these studies the Meeting concluded that the metabolism in ruminants is reasonably well understood. Even so, it would have preferred to see a higher proportion of the TRR identified in liver and kidney, since some of the unknown metabolites occurred at levels near or above some of those which were identified. For this reason and for further confirmation of proposed metabolic pathways, the Meeting concluded that a desirable extension to the work already done would be the analysis of any reserve (or future) cow liver and kidney samples for the two additional metabolites found in rats and for the thiobiuret (the major product formed in water under acidic conditions).

The Meeting confirmed the view of the 1991 JMPR that any future uses of buprofezin on major poultry feed items may require a more definitive poultry metabolism study.

The 1991 JMPR reviewed information on the metabolism in plants. On tomatoes buprofezin *per se* accounted for >90% of the residue after 7 days. In geoponic- or hydroponically-grown rice plants residues were taken up by the roots and translocated to other plant parts, the main residue being unchanged buprofezin and the major metabolite *p*-hydroxybuprofezin. In several other hydroponically-grown plants buprofezin was again the main residue, but the major metabolite was buprofezin sulfoxide, followed by the phenylbiuret. Because of these differences, the 1991 Meeting concluded that a study of metabolism by a major crop on which there was extensive use was needed, and required a citrus metabolism study. The 1991 JMPR also requested analysis for buprofezin sulfoxide, the phenylbiuret and *p*-hydroxybuprofezin in future field trials and for the thiobiuret in future metabolism or residue studies if it was found as a metabolite in citrus.

A citrus metabolism study was completed on glass-grown lemon trees at rates approximating GAP. Little translocation was found in immature fruit after applications of [^{14}C]buprofezin to leaves or stems. The manufacturer reported that the thiobiuret (BF-25), phenylbiuret (BF-11) and buprofezin sulfoxide (BF-10) were all used as reference standards in the study and were not detected. The one and two-dimensional TLC and HPLC analyses supported this with respect to buprofezin sulfoxide and the phenylbiuret, but none of the chromatograms of samples or standards provided confirmed analyses for the thiobiuret.

The Meeting concluded that there was little likelihood that significant levels of the phenylbiuret or buprofezin sulfoxide would be formed from topical applications to citrus and that this conclusion could reasonably be extended to other commodities for which temporary limits had been proposed, when taking into account the previously reviewed study on tomatoes. In view of the presence of significant levels of unidentified metabolites, proof that the thiobiuret was formed under acidic conditions and the lack of firm experimental evidence that it was not present in the citrus metabolism study, the Meeting had no basis to conclude that this compound is not formed during citrus metabolism.

As for other aspects of citrus metabolism, on day zero essentially all of the radioactivity was in or on the peel and 93-97% in the surface wash. After 14 days the proportion in the surface wash was reduced to 65% of the total and after 75 days to 16%. After these two periods the total residues in the peel (extractable + non-extractable) were 34.6 and were 82.9% respectively, indicating penetration from the surface into the peel with time. This was confirmed by the increase in the low pulp residue (from <0.4 to 1.3% of the total) over the same period.

After 14 days 66% of the TRR was unchanged buprofezin, 6% the dione metabolite (3-isopropyl-5-phenyl-1,3,5-thiadizinane-2,4-dione), 5.7% 2-amino-2-methylethyl-2-methylpropyl-4-phenylallophanate (designated as O or metabolite A), 3.6% unidentified metabolite B and 1.7% 1-isopropyl-3-phenylurea (IPU). After 75 days the levels were 18% buprofezin, 34% metabolite A, 9% metabolite B, 8% IPU and 7% dione.

On the basis of these findings the proposed metabolic pathway for plants is similar to, but more complex than, that outlined in the 1991 monograph. One route involves oxidation at the para position on the phenyl group to form hydroxybuprofezin, followed by cleavage of the heterocyclic ring to form hydroxy-IPU. A second route involves oxidation of the sulfur followed by ring cleavage to form the phenylbiuret, which is further degraded to IPU and oxidized to hydroxy-IPU.

In a third route oxidation of the *tert*-butylimino group to form the dione is followed by ring cleavage and formation of IPU, which is again oxidized to hydroxy-IPU. In the fourth route postulated hydroxylation of the *tert*-butyl group to an intermediate designated as BF-4 is followed by ring cleavage to give metabolite A, which is degraded to IPU and this again may be oxidized to hydroxy-IPU. In all cases the IPU may also be degraded to phenylurea.

Because of the multiple metabolic routes shown to occur in plants, future submissions of data on commodity groups other than fruiting vegetables and citrus should be accompanied by geoponic metabolism studies for the groups in question. The metabolism studies should be conducted before the field trials. If significant residues of additional metabolites are identified, field trials may need to include analyses for these as well.

Several extractability studies and analytical methods for buprofezin (including ICI method PPRAM 82) were provided in response to the requirement for validation of PPRAM 82, which was used for most of the trials reviewed by the 1991 JMPR. Several of the studies submitted to the present Meeting demonstrated that acetone (used in method 82) efficiently extracts buprofezin from fortified samples.

The primary response to the 1991 requirement was re-analysis of peaches which were found by PPRAM 82 in 1990 to contain 0.66 mg/kg buprofezin. The extraction procedures tested in the re-analysis were cold acetone, cold acetone/water, acetone reflux, cold methanol and methanol/water reflux. Results were similar in all cases, ranging from 0.52 to 0.78 mg/kg (mean 0.66 mg/kg), with 68-87% recoveries from 0.5 mg/kg fortifications.

The Meeting concluded that the available information sufficiently validated method 82 for the MRL levels recommended in 1991 (0.3 to 0.5 mg/kg), but agreed that additional validation was still desirable to allow an accurate estimate of a limit of determination. Full validation is needed for any future data developed with this method or others.

Another GLC method described for the determination of buprofezin and its dione and isopropylphenylurea metabolites has a limit of determination of 0.05 mg/kg in tomato products.

The 1991 JMPR required additional data from outdoor supervised trials on cucumbers and tomatoes if such uses were shown to be GAP, and additional data on oranges with analyses for *p*-hydroxybuprofezin, the thiobiuret, buprofezin sulfoxide and phenylbiuret in addition to buprofezin. Unchanged buprofezin had been the only significant residue in a tomato metabolism study. Data were provided for cucumbers, tomatoes and citrus.

Citrus. The temporary MRL of 0.3 mg/kg recommended for oranges by the 1991 JMPR was based mainly on Japanese trials, since other trials did not reflect maximum GAP conditions (trials in South Africa showed <0.05 mg/kg after 127 days but the GAP PHI is 90 days) or otherwise did not comply with GAP (too many applications or excessive rates). The 1991 Meeting considered maximum residues in the Japanese trials according to GAP to be approximately 0.3 mg/kg on a whole fruit basis, from a GAP application rate of 2.5 kg ai/ha (50 g ai/hl) and a 14-day PHI. Additional data from trials reflecting GAP were required.

The Meeting was informed that current Japanese GAP involves 5 applications at 25 g ai/hl and a 14-day PHI. Application rates are not on a kg ai/ha basis because that is volume-dependent and the volume varies according to the size of the trees. Therefore, it follows that the Japanese trials on oranges reviewed in 1991 were at twice GAP rates.

Additional citrus data from Brazil, Spain and Japan were provided to the Meeting in response to the 1991 requirement. In Brazilian trials the maximum residues in oranges were 0.04 mg/kg after 28 or 63 days and <0.01 mg/kg after 91 days from applications at 0.5 kg ai/ha (30 g ai/hl). Although the trials were according to FAO guidelines, buprofezin was reported not to be registered in Brazil and the data could not be related to the known GAP of other countries. The application rate was reported to be twice the "recommended" dosage, but it is within the range of GAP reported by some countries (either as g ai/ha or g ai/hl, not always both). Samples were adequately stored for the short period before analysis. The Meeting concluded that the Brazilian data were not sufficiently related to available GAP to estimate a maximum residue level.

In three Spanish trials maximum residues in whole oranges were 0.06 mg/kg after the Spanish 7-day GAP PHI, from an application rate of 1 kg ai/ha (25 g ai/hl), which was reported to be current Spanish GAP. This is an increase from the 10-12.5 g ai/hl rate reported as Spanish GAP in the 1991 JMPR monograph. The limit of determination for the HPLC determination was approximately 0.02 mg/kg in whole oranges for both buprofezin and *p*-hydroxybuprofezin. No residues (<0.02 mg/kg) of the latter were detected.

In a Japanese trial maximum residues on natsudaidais from GAP application rates were 0.7 and 0.4 mg/kg after 21 and 30 days respectively, the GAP PHI being 14 days. Five knapsack applications at GAP rates were made, each at 25 g ai/hl (1.25 kg ai/ha), to 2-tree plots. The trials were therefore within GAP but did not reflect the shortest GAP PHI. The reported limit of determination is 0.01 mg/kg for buprofezin and *p*-hydroxybuprofezin, but chromatograms suggest that 0.02-0.05 mg/kg may be more realistic.

Analytical samples from the Japanese trials stored at -20°C showed 80-106% recoveries of parent and *p*-hydroxybuprofezin after 58 days (pulp) or 90 days (peel). The field samples were stored at -10°C for periods ranging from 60 to 90 days for the shorter PHI samples to over twice that period for samples taken at longer intervals. Taken together with the good stability reported in 1991 of residues in apples, peaches and kiwifruit stored up to a year at -20°C, the Meeting concluded that the stability of stored samples in the Japanese trials was reasonably validated.

In the data submitted to the Meeting buprofezin residues in whole fruit were approximately 3 to 10 times those in the pulp, depending on the interval, which is consistent with the 3 to 8 times reported in the 1991 monograph. No residues of *p*-hydroxybuprofezin (<0.02 mg/kg) were detected in the peel, pulp or whole oranges in either the Spanish or Japanese trials. This is consistent with the metabolism study for this PHI and at the relative residue levels of buprofezin.

Although results have been provided from 14 supervised trials in 1991 and 1995 in 4 countries, few of them reflect GAP. The Japanese trials are the most significant because they most closely reflected maximum GAP conditions. The results from trials according to relevant GAP were South Africa, 1 trial, <0.05 mg/kg (4 results); Spain, 3 trials, 0.06 mg/kg, 2 x 0.0.03 mg/kg; Japan, 1 trial, 0.7, 0.4, 3 x 0.2, 0.08 mg/kg, giving altogether 0.7, 0.4, 0.2(3), 0.08, 0.06, <0.05(4) and 0.03(2) mg/kg.

The Meeting concluded that the available data were still insufficient to recommend an MRL for such a major commodity as citrus and recommended that the current temporary limit of 0.3 mg/kg be withdrawn. For future consideration of a citrus limit additional data reflective of GAP (including maximum application rates and shortest PHIs) need to be provided, together with confirmation of the current GAP, with labels in English or with an English translation, and all critical supporting information including a citrus processing study.

Cucumbers. The temporary MRL of 0.3 mg/kg estimated by the 1991 JMPR was based on data (mainly indoor) from The Netherlands, the UK, Greece and Japan. Maximum residues representing GAP were 0.06 mg/kg from The Netherlands (3-day PHI) and Greece (7-day PHI) and 0.21 mg/kg from trials according to proposed UK GAP (3-day PHI). Maximum residues reflecting GAP in a Japanese trial were 0.13 mg/kg after three days (the GAP PHI is 1 day), at 0.6 times the maximum permitted rate and 0.6 mg/kg at 1 day from a double rate. Residues were roughly proportional to the application rate. Because only the trials in Greece were outdoor, the Meeting required additional data from outdoor trials if outdoor uses are confirmed to be covered by GAP. Most of the GAP for cucumbers reported to the 1991 JMPR did not distinguish between field and glasshouse uses, but most of the trials were glasshouse.

No confirmation was received of non-glasshouse GAP for buprofezin uses on cucumbers, although uses listed by the 1991 JMPR for The Netherlands, the UK and Japan were confirmed (The Netherlands and UK confirmed as glasshouse uses). Accordingly there were no data from supervised field trials. However, additional data from trials according to GAP at four glasshouse sites in Japan were received. Residues at the 1-day Japanese GAP PHI were 0.4 to 0.8 mg/kg (mean 0.6 mg/kg), decreasing to a mean residue of 0.08 mg/kg after 7 days. On the basis of these new results, together with data reviewed by the 1991 JMPR, the Meeting recommended that the previous temporary MRL of 0.3 mg/kg should be replaced by an MRL of 1 mg/kg.

Tomatoes. The temporary MRL of 0.5 mg/kg recommended by the 1991 JMPR was based on trials in The Netherlands, the UK, Greece an Japan, with maximum residues reflecting GAP in The Netherlands of 0.2 mg/kg (0.3 mg/kg from a 1.3-fold rate) (GAP 0.075 kg ai/hl, 3-day PHI); UK 0.3 mg/kg (proposed GAP the same as The Netherlands) and Japan 0.4 mg/kg (GAP 1-1.9 kg ai/ha or 0.025 kg ai/hl). As with cucumbers, additional data would be required if field uses are confirmed to be GAP. GAP reported by the 1991 JMPR did not generally make a distinction, although most of the trials reviewed were glasshouse.

No specific information on GAP for field uses on tomatoes was provided to the Meeting, but additional data from Italy (field) and Japan (glasshouse) were provided. GAP in Germany, The Netherlands and the UK, and indirectly in Japan (where trials were reported as being according to GAP) was confirmed as applying to glasshouse uses. No GAP was provided for Italy, although the trials were within reported Japanese GAP. After 2 days (compared to the Japanese 1-day PHI) residues at the three Italian field locations ranged from 0.08 to 0.2 mg/kg, with no concentration reported in the juice and purée, although details of the processing were not given. No residues (<0.015 mg/kg) of *p*-hydroxybuprofezin were detected in any sample. Samples were stored appropriately to ensure their integrity.

The two applications in the Italian trials were also within the total seasonal application permitted in German GAP, although German GAP allows only one application. The rates expressed as kg ai/hl are also compatible with GAP rates reported in 1991 for Bulgaria, former Czechoslovakia, Jordan and Poland (Jordan and Poland have a 3-day PHI; the Italian results were at 2 or 7 days). The available results show a slow decrease in residues during the first 3 days. Although the Italian results cannot be strictly related to the GAP provided, they can be considered supplementary supportive information. Residues were generally lower than in the Japanese trials (see next para.), but the application rate expressed as kg ai/ha was higher in the latter, although the kg ai/hl rate is the same. A reasonable limit of determination for the HPLC method used would be 0.02 mg/kg.

Residues in the Japanese glasshouse trials according to GAP ranged from 0.3 to 0.7 mg/kg after 1 day, decreasing to 0.1 to 0.3 mg/kg after 7 days. Controls ranged from <0.005 to 0.04 mg/kg. An LOD of 0.05 mg/kg would appear to be reasonable for the method used (GLC with NP detection), according to chromatograms provided.

Taking into account residues from GAP applications up to 0.3 mg/kg in trials reviewed by the 1991 JMPR and up to 0.7 mg/kg in the new trials, the Meeting recommended that the previously recommended temporary MRL of 0.5 mg/kg should be replaced by an MRL of 1 mg/kg.

Processing tomatoes with field-incurred residues from exaggerated application rates revealed concentration factors of 23 and 34 from unwashed fruit to wet and dry pomace respectively. No significant concentration was observed in juice, purée or paste and residues of the dione metabolite did not exceed 0.02 mg/kg in dry pomace, even from more than twice the field application rate. No residues of the isopropylphenylurea metabolite were observed.

The JMPR reported no significant loss of buprofezin from apples, peaches and courgettes and only 13% from kiwi fruit after storage up to a year at -20°C. New information showed mean recoveries of 80-106% of both buprofezin and *p*-hydroxybuprofezin from 0.5 mg/kg fortification levels after storage of citrus for 56-58 days (pulp) or 91-93 days (peel) at -20°C. In cucumbers stored for 130 days at -20°C the recovery of buprofezin at 0.2 mg/kg fortification was reported as 90%. Mean recoveries of buprofezin added to tomatoes at 0.05 mg/kg ranged from 100 to 114% at four sites after storage for periods ranging from 53 to 94 days.

Residues in animals. The 1991 JMPR reviewed a conventional 28-day dairy cow feeding study which included feeding levels of 20 and 200 ppm in the diet. No residues of buprofezin (<0.01 mg/kg) were reported in muscle, kidney, liver, fat or milk from the low dose. On the basis of these results and the 0.5 and 0.3 mg/kg temporary limits recommended for tomatoes and oranges respectively, the 1991 Meeting tentatively concluded that residues of buprofezin *per se* were unlikely to occur in the muscle, kidneys, liver or milk of cattle, but recommended reconsideration of this conclusion in the light of required processing information and animal metabolism studies, which were provided to the present Meeting.

A 7-day metabolism study on a dairy cow was conducted at the equivalent of 27 ppm in the diet, a similar level to the 20 ppm feeding study reviewed by the 1991 JMPR. The metabolism study supports the finding in the feeding trial that residues of buprofezin are unlikely in the muscle, offal or milk of cattle at 20 ppm feeding levels. However, it also reveals that the main residue in animal products is *p*-hydroxybuprofezin (in the liver and kidneys) or *p*-acetamidophenol (in milk), not the parent compound determined in the feeding study. In the metabolism study, *p*-hydroxybuprofezin occurred at 0.13 mg/kg in liver, 0.07 mg/kg in kidney and <0.001 mg/kg in milk with lower levels of other metabolites. In milk the highest residue was *p*-acetamidophenol at 0.002 mg/kg. Residues in muscle were $\leq$ 0.02 mg/kg buprofezin equivalent and could not be identified.

The tomato processing study showed concentration of buprofezin by factors of 23 and 34 in wet and dry pomace respectively. With worst-case assumptions (e.g. residues at the proposed MRL level of 1 mg/kg in fruit, 34-fold concentration in dry tomato pomace, feeding levels of dry pomace of 25% of the diet in beef and 10% in dairy cattle) it can be estimated from the metabolism study that the main residue *p*-hydroxybuprofezin in cattle could occur at approximately 0.04 mg/kg in liver, 0.02 mg/kg in kidney and <0.001 mg/kg in milk, and *p*-acetamidophenol also <0.001 mg/kg in milk. Although no maximum residue level has been estimated for citrus, similar levels might be expected from the feeding of dry citrus pomace if the concentration factors are similar. Concentration in citrus pomace would be expected since most of the buprofezin residue has been shown to be in the peel. This observation and the concentration found in tomato pomace support the need for a citrus processing study.

Therefore, while the 1991 finding that no residues of buprofezin *per se* would be expected in meat, offal and milk was confirmed, there is a potential for low residues of *p*-hydroxy1buprofezin in liver and kidney. Although a conventional feeding trial has been conducted it was less useful than it might have been because only buprofezin was determined, not the residues likely to occur, mainly hydroxybuprofezin.

The guidance on the need for conventional feeding studies in the 1993 JMPR report requires feeding trials if detectable residues (>0.1 mg/kg) occur in feeds and metabolism studies indicate that residues may occur at levels >0.01 mg/kg. Even if it is assumed that residues in the whole fruit before processing into pomace are likely to be $\leq$ 50% of the MRL (generally true for tomatoes and citrus), the information on buprofezin indicates that an adequate conventional animal transfer study is required.

The Meeting therefore concluded that the available data were insufficient to estimate reliable maximum residue levels for animal products. The information required would include a conventional feeding trial in which the residues determined would include at least buprofezin and *p*-hydroxybuprofezin, and preferably also *p*-acetamidophenol in milk, with details of analytical methods. A suitable definition of the residue in animal products can be determined when these data are available, should it be decided that MRLs for animal products are needed.

Because a new metabolism study on citrus and new residue data on plants were available, the Meeting reconsidered the 1991 JMPR definition of the residue for regulatory purposes as buprofezin. The 1991 conclusion was based to a large extent on the tomato metabolism study showing over 90% of the residue in tomatoes to be unchanged buprofezin after 7 days.

The citrus metabolism study showed unchanged buprofezin to account for 66% of the residues after 14 days and 18% even after 75 days. After 75 days the main residue was shown to be metabolite A (2-amino-2-methylethyl-2-methylpropyl-4-phenylallophanate). No significant residues of buprofezin sulfoxide (reported in hydroponic metabolism studies) or the phenylbiuret or the thiobiuret metabolites were reported. However, as noted earlier, there was no experimental evidence provided to demonstrate that residues of the thiobiuret metabolite did not occur in citrus. In supervised trials data submitted to the Meeting no residues of *p*-hydroxybuprofezin were reported in citrus or tomatoes.

On the basis of these findings the Meeting confirmed the 1991 JMPR recommendation that the definition of the residue for regulatory purposes in cucumbers, tomatoes and oranges should be buprofezin. The Meeting was informed by the manufacturer that the definition of the residue for human foods of plant origin is buprofezin *per se* in Spain, The Netherlands, Belgium, Switzerland and Japan. The definition may need to be re-assessed if MRLs are proposed in the future for additional crop types (since metabolism varies among crops) or if the need is indicated when the desirable information listed below is provided.

buprofezin

RECOMMENDATIONS

The temporary maximum residue levels estimated by the 1991 JMPR are revised as shown below. The maximum residue levels estimated for cucumber and tomato are recommended for use as MRLs.

Definition of the residue: buprofezin

Commodity		Recommended MRL (mg/kg)		PHI (days) on which based
CCN	Name	New	Previous (temporary)	
VC 0424	Cucumber	1	0.3	1
VO 0448	Tomato	1	0.5	1
FC 0004	Oranges, sweet, sour	W[1]	0.3	21

1 Withdrawn

FURTHER WORK OR INFORMATION

Desirable

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

2. Further validation of PPRAM method 82 with sufficient chromatograms, recoveries and controls to permit an accurate estimate of the limit of determination.

3. Information on buprofezin and *p*-hydroxybuprofezin residues in food and commerce or at consumption, especially on buprofezin residues in commodities for which buprofezin uses are approved.

4. A conventional animal transfer study in which residues of buprofezin, *p*-hydroxybuprofezin and (in milk) *p*-acetamidophenol are determined, with suitable and validated analytical methods. Alternatively, reserve samples from the original transfer study can be analysed for these compounds if it can be convincingly demonstrated that such analyses would still be valid after prolonged storage. These studies are highly desirable, and would be required before maximum residue levels could be estimated for animal products.

5. Further information on national definitions of the residue for MRLs for crop and animal commodities.

6. Should citrus MRLs be contemplated in a future submission, the following further work or information would be:

   Desirable — Experimental evidence that the thiobiuret metabolite does not occur during citrus metabolism.

Required — 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 has been shown not to be formed during citrus metabolism).

REFERENCES

Bioanalytical Research Ltd., 1991. Buprofezin: Analysis of Assorted Crop Samples for storage stability. Unpublished Report No. 91/115/PC, September 1991.

Dick, J. and Rounds, L. 1984. Plant Protection Division Residue Analytical Method No. 82. The Determination of Buprofezin (PP618) Residues in Crops. Unpublished ICI report, December 13, 1984.

Huang, M. and Smith, S. 1995. Metabolism of [^{14}C]-Buprofezin in a Lactating Cow. Unpublished AgrEvo (Co. of Hoechst and NOR-AM) study 513BF, June, 13, 1995.

Iwamoto, T. and Kanauchi, M. 1994. Residue analysis of buprofezin in or on tomatoes applied three times with Applaud 25WP at 250 ppm (a.i.) Unpublished Report No. RES94-030, Japan Protection Association, Japan and Japan ECO-TECH Co., Ltd., Japan.

Iwamoto, T. and Matano, O. 1993. Residue determination of buprofezin in or on natsudaidais treated with Applaud 25 WP at 250 ppm (a.i.). Unpublished report No. R-1053, Japan Protection Association, Japan and the Institute of Environmental Toxicology, Japan.

Iwamoto, T. and Nishizawa, H. 1993. Residue determination of buprofezin in or on cucumbers treated with Applaud 25WP at 250 ppm (a.i.). Unpublished Report No. R-1052 from Japan Protection Association, Japan and Nihon Nohyaku Co., Ltd., Japan.

Kimura, Y. and Nishizawa, H. 1994. Confirmation of 1-*tert*-Butyl-3-isopropyl-5-phenyl-2-thiobiuret Formed by Hydrolysis of Buprofezin. Unpublished Nihon Nohyaku Co. Ltd. study, December 1994.

Leary, J., 1971. Gas Chromatographic Determination of Monitor (O,S-dimethyl phosphoramidothioate) Residues in Crops. J. Assoc. Off. Anal. Chem. 1971, 54, 1936.

Luke, M., Froberg, J., and Masumoto, H. 1975. Extraction and Cleanup of Organochlorine, Organophosphate, Organonitrogen and Hydrocarbon Pesticides in Produce for Determination by Gas-Liquid Chromatography. J. Assoc. Off. Anal. Chem. 1975, 58, 1020.

Luke, M., Froberg, J., Dosse, G. and Masumoto, H. 1981. Improved Multiresidue Gas Chromatographic Determination of Organophosphorus, Organonitrogen and Organohalogen Pesticides in Produce, Using Flame Photometric and Electrolytic Conductivity Detectors. J. Assoc. Off. Anal. Chem. 1981, 64, 1187.

Melkebeke, T. and Genijen, I. 1995a. Residues of buprofezin and p-hydroxy metabolite in oranges after application of buprofezin 25 in Spain. Unpublished report (NOTOX/BeBredelaar Project 122028) from NOTOX, The Netherlands.

Melkebeke, T. and Genijen, I. 1995b. Residues of buprofezin and p-hydroxy-metabolite in tomatoes and processing products after application of buprofezin 25WP in Italy. Unpublished Report (NOTOX Project 124649), NOTOX, The Netherlands.

Mills, P., Onley, J., and Gaither, R. 1963. Rapid Method for Chlorinated Pesticide Residues in Nonfatty Foods. J. Assoc. Off. Anal. Chem. 1963, 46, 186.

Neal, J. 1994. The Determination of Buprofezin Residues in Tomatoes by Gas Chromatography using Nitrogen Phosphorous Detection, RAM No. BF/06/94. (Appd. III to unpublished AgrEvo USA report BF-94R-02 (Neal, 1995).

Neal, J. 1995. At-harvest buprofezin-derived residues in or on processed tomato commodities following sequential applications of Applaud at an exaggerated rate, USA, 1994. Unpublished report No. BF-94R-02, AgrEvo USA, USA.

Nihon Nohyaku, 1985. Analytical Method of Buprofezin in Crops, soil and water. Unpublished Nihon Report.

Nishizawa, H., Shigemura, M., Suzuki, T. and Uchida, M. 1994. Simple Cleanup Procedure for Analysis of Buprofezin Residues and its Metabolite in Crops by Gas Chromatography (J. of AOAC International, Vol. 77, No. 6, 1994).

Nokata, M. 1995. Submission of data on buprofezin for evaluation by the 1995 JMPR. Letter, Nokata, M. to Murray, B., 3/14/95.

Olthof, P., 1995. Information of The Netherlands on pesticides to be considered by the 1995 JMPR, August 1994 (attachment to letter, Olthof to Ives, March 9, 1995).

Rieser, M. and Smith, S. 1995. Metabolism of [^{14}C]-Buprofezin in Citrus. Unpublished AgrEvo study No. 508BF, June 8, 1995.

Roberts-McIntosh, C. 1991. Extractability Study of Buprofezin Residues from Field Weathered Samples. Unpublished Bioanalytical Research Ltd. Report No. 91/116/PC.

Salgado, L. 1990. Buprofezin residues on/in orange fruits after application of applaud 25%WP. Unpublished report of Escola Superior de Agricultura de Lavras, Brazil.

CHLORPYRIFOS (017)

EXPLANATION

Chlorpyrifos was first evaluated in 1972 and has subsequently been reviewed a number of times. The use of chlorpyrifos on citrus fruit in the USA results in higher residues than the current CXL for citrus fruits, 0.3 mg/kg. Residue data on citrus would be made available to support a revision of the Codex MRL.

At the 21st Session of the CCPR in 1993 (ALINORM 93/24A para 251) chlorpyrifos was identified as a candidate for periodic review. It was listed as a candidate (but not yet scheduled) in the report of the 1995 CCPR (ALINORM 95/24A page 99, Annex 1 of Appendix IV).

Information was supplied by the manufacturer on physical properties, metabolism, analytical methods, frozen storage stability, use patterns, the effects of processing, and supervised trials on citrus fruit in the USA, Spain and South Africa. The Meeting reviewed the data relevant to the MRL for citrus fruits; other information is best reviewed in the context of the complete database in the periodic review programme.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Full details, with validation data, of the analytical methods used in studies of frozen storage stability, supervised residue trials and processing studies were made available to the Meeting.

Wetters (1973a,b) described a method for determining chlorpyrifos residues in sugar beet and processed fractions. The sample is extracted with acetone (liquid processed fractions with methanol) and cleaned up by a hexane-acetonitrile solvent partition and a silica gel column. Chlorpyrifos is determined by GLC with flame-photometric detection of phosphorus. The limit of determination was 0.01 mg/kg and recoveries from sugar beet leaves, roots, wet pulp, dry pulp and dry cake samples fortified at 0.01 to 1.0 mg/kg were in the range 79-112% (n = 48). Analytical recoveries from diffusion juice, thin juice and thick juice fortified at 0.01 to 1.0 mg/kg were in the range 94-116% (n = 31).

A similar method was used for chlorpyrifos residues in sorghum (Wetters, 1976), where the LOD was also 0.01 mg/kg. Analytical recoveries from sorghum grain, green plant, dry plant and silage fortified at 0.01 to 1.0 mg/kg were in the range 64-103% (n = 42). The method was also applied to oranges (Wetters, 1977). Analytical recoveries from whole oranges and orange peel + pulp fortified at 0.01, 0.1, 1.0 and 2.0 mg/kg were in the range 79-104% (n = 22). Orange juice samples were extracted by blending with methanol, but the solvent partition and column chromatography clean-up and GLC determination were as described above. Recoveries of chlorpyrifos from orange juice fortified at 0.01, 0.1 and 1.0 mg/kg were in the range 73-100% (n = 10).

Wetters (1978) provided additional information on analytical recoveries from whole oranges, orange peel, orange pulp and orange juice tested in the range 0.01-1.0 mg/kg. Recoveries were 82-99% (n = 20).

When orange substrates are heated with methanolic sodium hydroxide before extraction, any chlorpyrifos residues are converted to 3,5,6-trichloro-2-pyridinol (Wetters, 1977). The filtered methanol extract is concentrated to dryness and the residue taken up in water, acidified and partitioned with

benzene. The benzene extract is cleaned up on an alumina column and by solvent/bicarbonate and solvent/acid partitions. The trimethylsilyl derivative of 3,5,6-trichloro-2-pyridinol is formed by reaction with *N*,*O*-bis(trimethylsilyl)acetamide and determined by GLC with an ECD. The method measures the total residue, chlorpyrifos + 3,5,6-trichloro-2-pyridinol. When a duplicate sample is analysed for chlorpyrifos the level of 3,5,6-trichloro-2-pyridinol is estimated by difference. Analytical recoveries of 3,5,6-trichloro-2-pyridinol from whole oranges, orange peel + pulp, and orange juice fortified at 0.05, 0.1, 0.2, 1.0 and 2.0 mg/kg were in the range 80-104% (n = 18). Analytical recoveries of chlorpyrifos by this method on the same substrates fortified at 0.1 and 1.0 mg/kg were 73-88% (n = 6).

Wetters (1978) provided additional information on recoveries of 3,5,6-trichloro-2-pyridinol from whole oranges, orange peel, orange pulp and orange juice tested in the range 0.05-1.0 mg/kg: recoveries were 66-111% (n = 16).

Wetters (1985) extracted chlorpyrifos from oranges with methanol and cleaned up the extract on a C_{18} Sep-Pak. After a solvent partition into hexane the chlorpyrifos was determined by GLC with an FPD. The LOD was 0.01 mg/kg. Analytical recoveries of chlorpyrifos from samples fortified at 0.01-2.0 mg/kg ranged from 71 to 103% (n = 11). Analytical recoveries of 3,5,6-trichloro-2-pyridinol from samples fortified at 0.05-2.0 mg/kg by the previously described method were in the range 85-108% (n = 11).

Robb (1991) used the Wetters (1985) method for chlorpyrifos on oranges. Analytical recoveries from samples fortified at 0.01-1.0 mg/kg ranged from 83 to 96% (n = 12).

Chlorpyrifos residues were extracted from orange pulp and peel with dichloromethane in the presence of anhydrous sodium sulphate (Hollick and Sandenskog, 1976). Clean-up was effected by solvent partitioning and Florisil column chromatography. Chlorpyrifos residues were measured by GLC with an FPD. Analytical recoveries from pulp and peel fortified at 0.01-1.0 mg/kg ranged from 81 to 112% (n = 14). The same method was used by Hollick and Walker (1976) with chlorpyrifos recoveries in the range 87-115% (n = 8).

Wetters (1981) reported the analytical methods for chlorpyrifos and 3,5,6-trichloro-2-pyridinol used in supervised trials and processing studies on grapefruit, lemons, oranges and tangelos. The methods had already been described in other studies; variations were mostly in the initial extraction, which depends on the nature of the substrate. Analytical recoveries of chlorpyrifos at fortification levels from 0.01 to 1.0 mg/kg from whole fruit, dried citrus pulp, molasses, juice, press liquor, peel frits, finisher pulp, chopped residue and citrus oil (the last tested up to 5.0 mg/kg) were in the range 55 to 116% (n = 103). Analytical recoveries of 3,5,6-trichloro-2-pyridinol at fortification levels of 0.05 to 1.0 mg/kg from citrus fruit and process fractions were in the range 78 to 102% (n = 64).

Stability of pesticide residues in stored analytical samples

Information on the frozen storage stability of chlorpyrifos and 3,5,6-trichloro-2-pyridinol residues in a range of raw agricultural and processed commodities was made available to the Meeting.

Wetters (1990) summarized the results of studies of the stability of chlorpyrifos residues on various substrates when stored frozen (Table 1). Chopped samples fortified with chlorpyrifos and 3,5,6-trichloro-2-pyridinol were kept in freezer storage and analysed periodically. The validated LOD for chlorpyrifos by a GLC method with FP detection was 0.01 mg/kg, and for 3,5,6-trichloro-2-pyridinol with EC detection 0.05 mg/kg. In some cases samples were heated with alcoholic sodium hydroxide before extraction, which converted chlorpyrifos to the pyridinol and allowed determination of the total residue.

Table 1. Stability of residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in various substrates stored at -18°C (Wetters 1990).

Commodity	Container	Storage interval, days	Chlorpyrifos		Trichloropyridinol	
			Fortification mg/kg	% remaining	Fortification mg/kg	% remaining
Alfalfa, green forage	glass	327 340 346	1.0 1.0	110, 71 100	0.20 0.20	80 70,75
Alfalfa hay	glass	327 340 346	1.0 1.0	110 71[1] 100	0.20 0.20	80 70 75
Almond hulls	glass	258	0.10	57[1]	0.10	78
Almond kernels	glass	258	0.10	82[1]	0.10	74
Apple	glass	172 258 271	0.10 0.10 0.10	93 79[1] 90	 0.10	 82
Apple	polyethylene	1351 1533	1.0 1.0	90 105[1] 80 68[1]	1.0 1.0	61 99
Apple	glass	258	0.10	79[1]	0.10	82
Apricots	glass	258	0.10	84[1]	0.10	74
Cherries	glass	260 272	0.10	102[1]	0.10 0.10	82 88
Maize, cobs	glass	30 150	0.10 0.10	91 74 95[1]		
Maize, grain	glass	30 150 810 810	0.10 0.10 0.10 1.0	81 82 98[1] 85 70		
Maize, green plant	glass	30 150 150 810 810	0.10 0.10 0.10 0.10 1.0	82 89 83 84 96[1] 82[1] 81 73		
Maize, stalks	glass	30 150 810 810	0.10 0.10 0.10 1.0	86 85 98[1] 104 76		
Orange juice	glass	162	0.10	79		
Orange peel + pulp	glass	162 172	0.10	103	 0.20	 87
Oranges	glass	162 172	0.10 0.10	78 79	 0.20	 87 87
Peaches	glass	258	0.10	73[1]	0.10	70
Pears	glass	258	0.10	75[1]	0.10	74
Plums	glass	258	0.10	98[1]	0.10	72
Sorghum, dry plant	glass	61 80	1.0 1.0	83 76[1]	 0.20	 86
Sorghum, fodder	polyethylene	1679 1716	1.0 1.0	92 109[1]	 1.0	 103
Sorghum, grain	glass	65 82	1.0 1.0	77 75[1]	 0.20	 83
Sorghum, grain	polyethylene	1679 1716	1.0 1.0	76 91[1]	 1.0	 93
Sorghum, green plant (silage stage)	glass	65 82	1.0 1.0	77 69[1]	0.20	82
Sorghum, green plant	glass	61 80	1.0 1.0	88 74[1]	 0.20	 71

Commodity	Container	Storage interval, days	Chlorpyrifos		Trichloropyridinol	
			Fortification mg/kg	% remaining	Fortification mg/kg	% remaining
Sugar beet roots	polyethylene	1369	1.0	82[1]	1.0	108
Sugar beet lime cake	glass	68 75 80 96	1.0 1.0 1.0	53 38 93[1]	 0.10	 83
Sugar beet tops	polyethylene	1369	1.0	91[1]	1.0	77
Sugar beet dry pulp	glass	68 96	1.0	88	 0.10	 82
Sugar beet wet pulp	glass	68 96	1.0 0.10	91	 0.10	 80
Sugar beet leaves	glass	38 48 147 151 151 169	 0.10 0.10 0.10 1.0	 88 90 69 77[1] 85 80[1]	0.10 0.10 1.0 0.10	88 111 102 88
Sugar beet roots	glass	38 48 147 151 151 169	 0.10 0.10 0.10 1.0	 74 89 73 68[1] 63 71[1]	0.10 0.10 1.0 0.10	91 128 87 88
Sugar beet thin juice	glass	69 96	1.0	92	0.10	82
Sugar beet diffusion juice	glass	69 96	1.0	93	0.10	83
Sugar beet thick juice	glass	69 96	1.0	90	0.10	82
Sweet corn, kernels	glass	30 150	0.10 0.10	97 84 100[1]		
Sweet corn, green plant	glass	30 150 150	0.10 0.10 0.10	96 90 84 76 80[1] 80[1]		
Sweet corn, kernels + cobs	glass	30 150	0.10 0.10	96 80 86[1]		
Sweet corn, husks	glass	30 150	0.10 0.10	93 79 89[1]		
Sweet corn, cobs + husks	glass	30 150	0.10 0.10	95 80 91[1]		
Sweet potatoes	glass	1 3 40.10 0.10	72 89[1]	 0.10	 92	
Tomatoes	glass	51 175	0.10 0.10	70 96[1] 90 91	0.10	92
Walnuts	glass	258	0.10	77[1]	0.10	80

[1] Determined as 3,5,6-trichloro-2-pyridinol following hydrolysis

USE PATTERN

Information was made available to the Meeting on registered uses of chlorpyrifos on citrus in South Africa, Spain and the USA. The uses are shown in Table 2.

Chlorpyrifos is registered for use in the USA on citrus fruits for the control of aphids, avocado leafroller, black scale, brown soft scale, California red scale, chaff scale, citrus rust mites, cutworms, Florida red scale, fruit tree leafroller, grasshoppers, katydids, Lepidopterous larvae, long scale, mealybugs, orange tortrix, orange dogs, purple scale, scale insects, snow scale, thrips, and western tussock moth. A petroleum spray oil recommended for use on citrus trees may be added to dilute spray mixtures to improve the control of aphids, mealybugs, scale insects and thrips. Chlorpyrifos is also recommended for the control of imported fire ants and other ant species by application to orchard floors.

Table 2. Registered uses of chlorpyrifos on citrus.

Used on	Country	Form	Application				PHI, days
			Method	Rate per applic, kg ai/ha	Spray conc, kg ai/hl	No.	
Citrus crop	South Africa	EC	High vol.	1.4-2.4	0.0096-0.048	1-2	60
Citrus crop	Spain	EC	High vol.	2.9-4.8	0.075-0.10	1-2	21
Citrus crop	USA	EC	airblast	3.4-6.7	0.015-0.72	1-2	35
Citrus crop	USA	EC	airblast	1.1-3.9	0.010-0.42	1-2	21
Citrus crop	USA	EC	aerial or airblast	1.1-3.9	0.80-2.1	1-2	21
Citrus orchard floor	USA	EC	ground boom	0.84-1.1	0.36-0.48	10	28

RESIDUES RESULTING FROM SUPERVISED TRIALS

Data from supervised trials on citrus fruits are shown in Tables 3 to 7.

Table 3.Oranges. USA, South Africa.
Table 4.Mandarins. Spain.
Table 5.Lemons. USA.
Table 6.Grapefruit. USA.
Table 7.Tangelos. USA.

Wetters (1977) reported the results of chlorpyrifos residue trials on oranges in California (Table 3, GH-C 1041). Chlorpyrifos was applied once as either a high- or low-volume spray. In the first trial there were 36 trees per treatment and 4 samples were taken representing single tree replicates. In the second trial there were 12 trees per treatment and the 4 samples were taken by random selection of one fruit from each quadrant of 6 trees. In the third trial a sample was taken by randomly selecting 6 fruit from each quadrant of a tree (single tree plots and 4 replicates per treatment).

Chlorpyrifos was applied to orange trees in a high-volume treatment reported by Wetters (1978). Samples were taken from each of 6 trees (4 quadrants per tree) within the treated plot, one sample per set of 6 quadrants. The results are shown in Table 3 (GH-C 1141).

Wetters (1985) reported the comparison of residues arising from the high- and low-volume foliar application of chlorpyrifos to orange trees both with and without spraying oils. The results are shown in Table 3 (GH-C 1724). In one trial 4 separate trees were sampled per treatment, and in the other a replicate sample was taken from each ¼ row (0.6 ha per plot).

Robb (1991) measured the chlorpyrifos residues in oranges after 3 foliar applications and 2 orchard floor applications (Table 3, 89078). Samples were taken from the centre trees of each of the 4 test plots.

Wetters (1981) reported a series of supervised residue and processing trials in the USA on oranges, lemons, grapefruit and tangelos. The results are shown in Tables 3, 5, 6, 7 and 9 (GH-C 1441).

Plot sizes ranged from 36 trees up to 1 acre (0.4 ha). Chlorpyrifos was applied by oscillating boom citrus sprayers, handgun sprayers or airblast sprayers for high-volume treatments and by specialized sprayers for low-volume treatments.

Hollick and Sandenskog (1976) described supervised trials with high-volume chlorpyrifos applications to oranges in South Africa (Table 3, GHE-P-413). The oranges were peeled, the weight of pulp and peel recorded and the pulp and peel analysed separately. The level of chlorpyrifos in the whole fruit was calculated from these analyses and the relative weights. Hollick and Walker (1976) reported a further trial (GHE-P-414) with 3 treatments at 2-monthly intervals.

Mandarin trees in Spain were treated with a high-volume application of chlorpyrifos in a supervised trial in 1992 (Khoshab *et al*., 1993). The plot size was 4 trees with fruit for analysis taken randomly from all parts of trees. The results are shown in Table 4.

Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are corrected for controls and average % recoveries. Residues in the Tables are generally rounded to 2 significant digits except those close to the LOD which are rounded to 1 significant digit.

Table 3. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in whole oranges from foliar applications of chlorpyrifos in supervised trials in South Africa and the USA. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application				PHI, days	Residues, mg/kg[1]		Ref.
	Form	kg ai/ha	kg ai/hl	No.		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
USA (CA), 1975 (Valencia)	EC	12	0.090	1	14	0.40 0.55 0.49 0.36	0.10 <0.05 <0.05 <0.05	GH-C 1041
USA (CA), 1975 (Valencia)	EC	12	1.3	1	14	1.2 1.0 1.1 1.1	0.58 0.30 0.1 0.32	GH-C 1041
USA (CA), 1975 (Valencia)	EC	15	0.090	1	14	0.86 0.84 0.77 0.80	0.18 0.38 0.09 0.45	GH-C 1041
USA (CA), 1975 (Valencia)	EC	15	1.6	1	14	0.56 0.47 0.82 0.24	<0.05 0.13 <0.05 0.08	GH-C 1041
USA (CA), 1975 (Valencia)	EC	17	0.090	1	0 3 14 30	1.5 1.6 1.5 1.3 0.54 2.6 0.60 0.57 0.38 0.70 0.52 0.35 0.21 0.21 0.13 0.18	<0.05(3) 0.08	GH-C 1041
USA (CA), 1975 (Valencia)	EC	17	1.8	1	0 3 14 30	6.8 5.1 7.1 3.3 3.8 3.7 3.6 1.8 3.3 2.0 2.3 0.70 0.80 0.69 0.89 0.63	<0.05 0.14 0.32 0.62	GH-C 1041
USA (CA), 1978 (Valencia)	EC	8.4	0.060	1	14 21	0.19 0.20 0.15 0.12 0.12 0.093	<0.05 <0.05 0.05 <0.05(3)	GH-C 1441
USA (CA), 1978 (Valencia)	EC	8.4	0.90	1	14 21	0.65 0.57 0.45 0.34 0.46 0.35	0.05 <0.05 0.35 0.09 0.05 0.13	GH-C 1441
USA (CA), 1978 (Valencia)	EC	14	0.060	1	14 21	0.29 0.30 0.29 0.16 0.18 0.19	0.16 <0.05 0.07 0.06 0.10 <0.05	GH-C 1441
USA (CA), 1978 (Valencia)	EC	14	1.5	1	14 21	2.3 2.1 2.2 1.7 1.9 1.0	0.43 0.49 0.32 <0.05 0.39 0.25	GH-C 1441
USA (CA), 1978 (Valencia)	EC	8.0	0.060	1	14 21	0.30 0.28 0.33 0.33 0.34 0.44 0.35 0.27	<0.05(4) <0.05(4)	GH-C 1141
USA (CA), 1978 (Valencia)	EC	11	0.060	1	14 21	0.59 0.56 0.58 0.46 0.47 0.44 0.44 0.52	<0.05(4) <0.05(4)	GH-C 1141
USA (FL), 1979 (Valencia)	EC	4.4	0.030	2	14	0.30 0.34 0.29 0.31	0.05 0.08 <0.05 <0.05	GH-C 1441

Country, year (variety)	Application				PHI, days	Residues, mg/kg[1]		Ref.
	Form	kg ai/ha	kg ai/hl	No.		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
USA (FL), 1979 (Valencia)	EC	8.6	0.060	2	14	0.51 0.57 0.68 0.74	0.15 0.26 <0.05 0.12	GH-C 1441
USA (TX), 1979 (Valencia)	EC	1.4	0.060	1	13 13 21 21	0.065 0.05 0.074 0.04 0.05 0.05 0.098 0.05 0.065 0.05 0.062 0.05	<0.05(3) <0.05(3) <0.05(3) <0.05(3)	GH-C 1441
USA (TX), 1979 (Valencia)	EC	1.4	0.20	1	13 21	0.34 0.47 0.45 0.38 0.49 0.34	0.05 <0.05 0.05 <0.05(3)	GH-C 1441
USA (CA), 1984 (Navel)	EC	6.7	0.048	1	35	0.38 0.35 0.36 0.30	0.07 0.06 <0.05 0.05	GH-C 1724
USA (CA), 1984 (Navel)	EC + oil	6.7	0.048	1	35	0.41 0.32 0.37 0.23	<0.05 0.07 <0.05 <0.05	GH-C 1724
USA (CA), 1984 (Navel)	EC + oil	6.7	0.048	1	35	0.39 0.36 0.33 0.36	<0.05 0.09 <0.05 0.05	GH-C 1724
USA (CA), 1984 (Navel)	EC	3.9	0.42	1	21	1.3 0.61 0.65 0.99	0.36 0.16 0.08 0.07	GH-C 1724
USA (CA), 1984 (Navel)	EC + oil	3.9	0.42	1	21	2.0 1.0 1.0 1.3	0.40 0.23 <0.05 0.34	GH-C 1724
USA (CA), 1983 (Valencia)	EC	6.7	0.048	1	36	0.21 0.21 0.26 0.25	0.06 0.07 0.11 <0.05	GH-C 1724
USA (CA), 1983 (Valencia)	EC + oil	6.7	0.048	1	36	0.075 0.063 0.071 0.093	<0.05(3) 0.07	GH-C 1724
USA (CA), 1983 (Valencia)	EC + oil	6.7	0.048	1	36	0.11 0.097 0.10 0.05	0.09 0.07 0.07 0.08	GH-C 1724
USA (CA), 1983 (Valencia)	EC	3.9	0.42	1	21	0.23 0.38 0.15 0.24	<0.05 <0.05 0.12 <0.05	GH-C 1724
USA (CA), 1983 (Valencia)	EC + oil	3.9	0.42	1	21	0.28 0.25 0.36 0.15	0.12 0.10 0.06 0.05	GH-C 1724
USA (CA), 1990 (Valencia)	EC	13 +4.5 +13	1.4 +0.47 +1.4	3	28	0.28 0.33 0.42 0.51		89078
USA (CA), 1990 (Valencia)	EC	13 +4.5 +13	1.4 +0.47 +1.4	3	28	0.60 0.49 0.30 0.38		89078
South Africa, 1975 (Navel)	EC		0.05	1	7 33 62 91	0.21 f<0.01 p0.53 0.10 f<0.01 p0.28 0.05 f<0.01 p0.13 0.03 f<0.01 p0.10		GHE-P-413
South Africa, 1975 (Navel)	EC		0.05	1	7 31 59 92	0.45 f<0.01 p1.5 0.20 f<0.01 p0.59 0.12 f<0.01 p0.33 0.05 f<0.01 p0.15		GHE-P-413
South Africa, 1975 (Navel)	EC		0.10	1	7 31 59 92	0.59 f<0.01 p2.0 0.29 f<0.01 p0.68 0.17 f<0.01 p0.57 0.12 f<0.01 p0.33		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.05	1	7 31 59 92	0.56 f<0.01 p2.3 0.32 f<0.01 p1.1 0.14 f<0.01 p0.45 0.06 f<0.01 p0.21		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.10	1	7 31 59 92	0.72 f<0.01 p2.5 0.45 f<0.01 p1.5 0.27 f<0.01 p0.93 0.17 f<0.01 p0.60		GHE-P-413

Country, year (variety)	Application				PHI, days	Residues, mg/kg[1]		Ref.
	Form	kg ai/ha	kg ai/hl	No.		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
South Africa, 1975 (Valencia)	EC		0.05	1	7 30 58 86	0.37 f<0.01 p0.99 0.25 f<0.01 p0.80 0.21 f<0.01 p0.70 0.13 f<0.01 p0.41		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.10	1	7 30 58 86	0.62 f<0.01 p1.7 0.54 f<0.01 p1.7 0.55 f<0.01 p1.6 0.29 f<0.01 p0.84		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.05	2	31 61 91	0.21 f<0.01 p0.62 0.19 f<0.01 p0.61 0.13 f<0.01 p0.46		GHE-P-413
South Africa, 1975 (Valencia)	EC		0.05 +0.02	2	190	0.07 f<0.01 p0.22		GHE-P-413
South Africa, 1976 (Valencia)	EC		0.06+ 2×0.03	3	26 48 80 102 116	0.39 f<0.01 p1.1 0.26 f<0.01 p0.75 0.26 f<0.01 p0.75 0.25 f<0.01 p0.69 0.28 f<0.01 p0.81 c0.05 c0.04 c0.03 c0.04		GHE-P-414

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for control and average recoveries

f: pulp p: peel c: control sample

Table 4. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in mandarins from foliar applications of EC formulations of chlorpyrifos in supervised trials in Spain. Underlined residues are from treatments according to GAP.

Year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
1992 (Clemenules)	2.9	0.096	1	1 27 56 89 116	1.4 0.40 0.27 0.17 0.14 f<0.01 p0.43	1.1 0.40 0.25 0.20 0.12 f<0.05 p0.36	R92-12
1993 (Hernandina)	2.9	0.096	1	22	0.89 0.75 0.99 0.81		R93-06A
1993 (Clemenules)	2.9	0.096	1	22	1.2		R93-06B
1993 (Nova)	3.8	0.096	1	24	0.55		R93-06C

f: pulp p: peel

Table 5. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in lemons from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA.

State, year (variety)	Application			PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
CA, 1978 (Lupe)	6.7	0.060	1	19 26	0.18 0.094 0.13 0.12 0.12 0.096	<0.05 <0.05 0.07 0.06 0.08 0.05	GH-C 1441
CA, 1978 (Lupe)	6.7	0.72	1	19 26	0.04 0.059 0.062 0.03 0.055 0.04	<0.05(3) <0.05(3)	GH-C 1441
CA, 1978 (Lupe)	8.4	0.060	1	14 21	0.27 0.30 0.31 0.20 0.21 0.22	0.06 <0.05 <0.05 0.06 0.08 0.06	GH-C 1441
CA, 1978 (Lupe)	8.4	0.90	1	14 21	0.17 0.16 0.18 0.14 0.16 0.14	<0.05(3) 0.05 0.05 0.05	GH-C 1441
FL, 1980 (Bearss)	5.8	0.030	2	14	0.27 0.28 0.19	0.14 0.09 0.16	GH-C 1441
FL, 1980 (Bearss)	12	0.060	2	14	0.39 0.31 0.49	0.19 0.20 0.06	GH-C 1441

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Table 6. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in grapefruit from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA. Underlined residues are from treatments according to GAP.

State, Year (variety)	Application			PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
FL, 1980 (Marsh)	2.9	0.029	2	14	0.38 0.31 0.32	<0.05(3)	GH-C 1441
FL, 1980 (Marsh)	5.9	0.060	2	14	0.52 0.45 0.57	<0.05 0.09 0.08	GH-C 1441
TX, 1979 (Ruby Red)	1.4	0.060	1	13 21	0.03 0.03 0.04 0.067 0.03 0.05	<0.05(3) <0.05(3)	GH-C 1441
TX, 1979 (Ruby Red)	1.4	0.20	1	13 21	0.23 0.38 0.27 0.21 0.31 0.30	0.15 <0.05 0.13 <0.05 0.17 0.07	GH-C 1441
TX, 1979 (Webb Redblush)	1.4	0.060	1	13 21	0.04 0.05 0.04 0.03 0.05	<0.05(3) <0.05(3)	GH-C 1441
TX, 1979 (Webb Redblush)	1.4	0.20	1	13 21	0.26 0.36 0.21 0.34 0.20 0.15	0.06 <0.05 0.05 <0.05 0.06 <0.05	GH-C 1441

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Table 7. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in tangelos from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA.

State, year (variety)	Application			PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl	No.		Chlorpyrifos	3,5,6-trichloro-2-pyridinol	
FL, 1980 (Orlando)	4.4	0.030	2	14	0.43 0.50 0.45	0.13 0.07 <0.05	GH-C 1441
FL, 1980 (Orlando)	8.6	0.060	2	14	0.68 0.74 0.60	<0.05 <0.05 0.06	GH-C 1441

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

FATE OF RESIDUES IN STORAGE AND PROCESSING

In processing

Information was made available to the Meeting on the fate of field-incurred chlorpyrifos residues during the processing of oranges, grapefruit, lemons and tangelos.

Wetters (1977) reported the results of chlorpyrifos processing trials (Table 8, GH-C 1041) on oranges in California. Chlorpyrifos was applied once as a high- or low-volume spray. Oranges were cut in half and juiced in a stainless steel electric juicer on a laboratory scale.

In the processing trials of 1978 (Table 8, GH-C 1141) oranges were peeled manually and juice was prepared in the laboratory directly from the peeled oranges with a Hobart juice extractor (Wetters 1978).

Wetters (1981) processed batches of 10-15 field boxes of citrus fruit according to the scheme in Figure 1, simulating the commercial process. Residues in the unwashed fruit and fractions through to the citrus juices and oils are shown in Table 9.

Table 8. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in orange juice, peel and pulp from foliar applications of EC formulations of chlorpyrifos in supervised trials in the USA and subsequent processing through a juicer (Wetters 1977, 1978).

State, year (variety)	Application		PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
Orange peel + pulp						
CA, 1975 (Valencia)	12	0.090	14	0.52 0.56 0.55 0.51	0.17 0.16 0.13 0.16	GH-C 1041
CA, 1975 (Valencia)	12	1.3	14	1.6 1.5 1.4 1.3	0.27 <0.05 0.26 0.06	GH-C 1041
CA, 1975 (Valencia)	15	0.090	14	1.5 1.6 1.5 1.7	0.25 0.31 0.28 0.27	GH-C 1041
CA, 1975 (Valencia)	15	1.6	14	0.59 0.85 0.62 0.60	0.06 0.15 0.07 0.20	GH-C 1041
CA, 1975 (Valencia)	17	0.090	0 3 14 30	3.2 2.4 1.5 1.0 0.88 0.69 0.40 0.39	 0.16 0.13	GH-C 1041
CA, 1975 (Valencia)	17	1.8	0 3 14 30	16 5.4 8.4 4.6 2.0 4.9 1.4 0.68	 0.13 0.15	GH-C 1041
ORANGE PEEL						
CA, 1978 (Valencia)	8.0	0.060	14 21	1.0 0.98 1.0 1.0 0.97 0.84 0.92 0.89	0.05 0.08 <0.05 <0.05 <0.05 0.06 0.09 <0.05	GH-C 1141
CA, 1978 (Valencia)	11	0.060	14 21	1.9 1.9 2.0 1.6 2.1 1.9 1.7 1.7	0.06 <0.05 0.11 <0.05 <0.05 <0.05 0.08 0.16	GH-C 1141
ORANGE PULP						
CA, 1978 (Valencia)	8.0	0.060	14 21	0.03 0.02 0.03 0.01 0.01 0.01 0.01 0.02	<0.05(4) <0.05(4)	GH-C 1141
CA, 1978 (Valencia)	11	0.060	14 21	0.055 0.03 0.04 0.067 0.02 0.068 0.02 0.02	<0.05(4) <0.05(4)	GH-C 1141
ORANGE JUICE						
CA, 1975 (Valencia)	12	0.090	14	0.01 0.01 0.01 0.01	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	12	1.3	14	0.074 0.03 0.02 0.02	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	15	0.090	14	0.01 <0.01 0.01 0.01	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	15	1.6	14	<0.01 0.01 <0.01 <0.01	<0.05(4)	GH-C 1041
CA, 1975 (Valencia)	17	0.090	0 3 14 30	0.04 0.05 0.02 0.02 0.01 0.01 0.02 0.01	 <0.05(2)	GH-C 1041

State, year (variety)	Application		PHI, days	Residues, mg/kg[1]		Ref.
	kg ai/ha	kg ai/hl		chlorpyrifos	3,5,6-trichloro-2-pyridinol	
CA, 1975 (Valencia)	17	1.8	0 3 14 30	0.78 0.071 0.22 0.11 0.17 0.062 0.05 0.03	 <0.05(2)	GH-C 1041
CA, 1978 (Valencia)	8.0	0.060	14 21	<0.01 0.01 <0.01 <0.01 <0.01 0.01 <0.01 0.01	<0.05(4) <0.05(4)	GH-C 1141
CA, 1978 (Valencia)	11	0.060	14 21	<0.01 (4) 0.01 0.01 0.01 0.01	<0.05(4) <0.05(4)	GH-C 1141

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Figure 1. Citrus processing (Wetters, 1981)

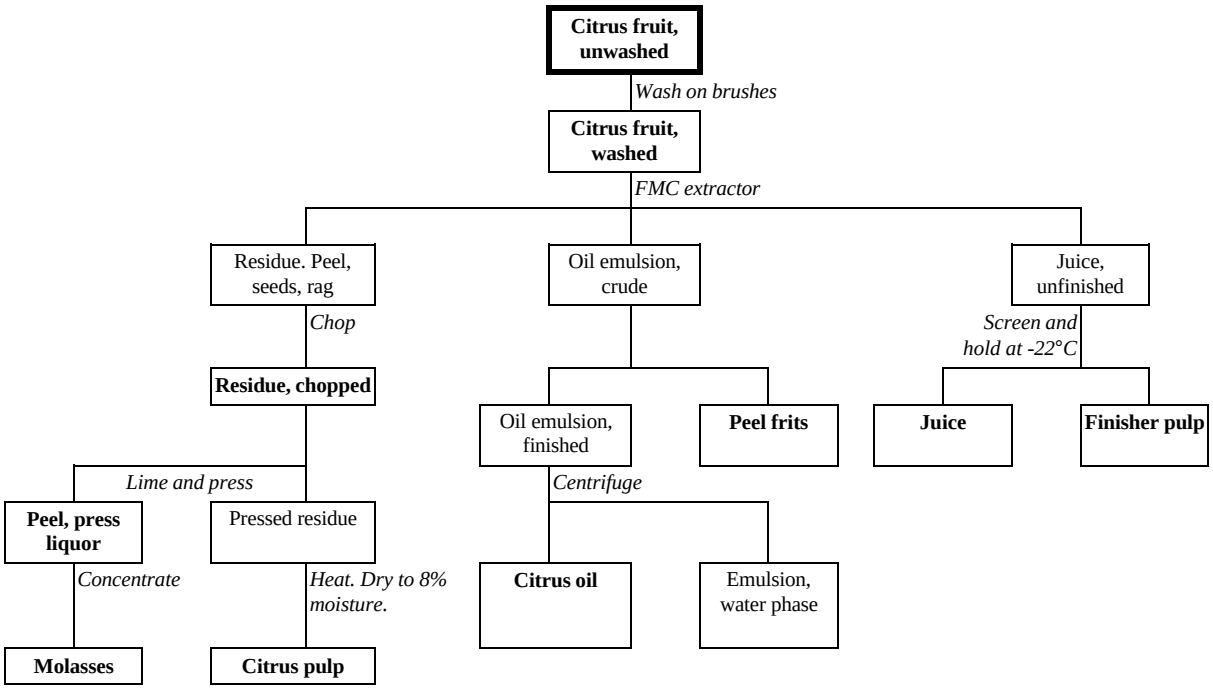


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Table 9. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in citrus and process fractions from foliar application of chlorpyrifos in supervised processing trials in the USA (Wetters, 1981, ref. GH-C 1441). Note that "citrus pulp" is a commercial processing fraction derived from the extractor residue, peel, seeds and rag.

Commodity, state, year, (variety), treatment	Residues, mg/kg[1]	
	Chlorpyrifos	3,5,6-trichloro-2-pyridinol
Grapefruit, FL, 1979 (Marsh). 2×5.9 kg ai/ha. 15 days PHI.		
Whole grapefruit, unwashed	0.36	0.07
Whole grapefruit, washed	0.29	<0.05
Citrus pulp, dried	1.1	0.36
Molasses	0.18	0.09
Juice	<0.01	<0.05
Press liquor	0.074	<0.05
Peel frits	1.3	0.07
Pulp, finisher	<0.01	<0.05
Chopped residue, peel	0.50	0.11
Oil	6.3	<0.05
Lemon, FL, 1978 (Bearss). 2×5.8 kg ai/ha. 14 days PHI.		
Whole lemons, unwashed	0.38	0.07
Whole lemons, washed	0.31	0.12
Citrus pulp, dried	0.48	0.46
Molasses	0.058	0.35
Juice	<0.01	<0.05
Press liquor	0.082	<0.05
Peel frits	0.71	0.21
Pulp, finisher	0.01	<0.05
Chopped residue, peel	0.20	0.13
Oil	1.0	<0.05
Orange, FL, 1979 (Valencia). 2×8.6 kg ai/ha. 15 days PHI.		
Whole oranges, unwashed	0.51	0.15
Whole oranges, washed	0.47	0.18
Citrus pulp, dried	1.2	0.45
Molasses	0.059	0.24
Juice	<0.01	<0.05
Press liquor	0.16	<0.05
Peel frits	1.5	0.37
Pulp, finisher	0.02	<0.05
Chopped residue, peel	0.69	0.21
Oil	3.0	0.27
Tangelo, FL, 1979 (Orlando). 2×4.5 kg ai/ha. 15 days PHI.		
Whole tangelos, unwashed	0.59	<0.05
Whole tangelos, washed	0.92	<0.05
Citrus pulp, dried	1.7	0.08
Molasses	0.05	0.10

Commodity, state, year, (variety), treatment	Residues, mg/kg[1]	
	Chlorpyrifos	3,5,6-trichloro-2-pyridinol
Juice	<0.01	<0.05
Press liquor	0.36	0.05
Peel frits	3.6	0.28
Pulp, finisher	0.082	<0.05
Chopped residue, peel	1.1	0.19
Oil	5.6	0.48

[1] Chlorpyrifos residues are not corrected for recovery. Residues of 3,5,6-trichloro-2-pyridinol are calculated by difference (total minus the 3,5,6-trichloro-2-pyridinol contributed by the alkaline hydrolysis of chlorpyrifos) and are corrected for controls and average recoveries

Residues in the edible portion of food commodities

In a series of supervised trials in South Africa in 1975-76 (reports GHE-P-413 and GHE-P-414 in Table 3) the pulp and peel of oranges were analysed separately. Chlorpyrifos residues were not detected (<0.01 mg/kg) in any of the pulp samples including those from fruit treated at exaggerated rates or harvested at intervals less than the official PHI. Residues in the whole fruit ranged from 0.03 to 0.72 mg/kg (median 0.25 mg/kg, n = 37).

In a Spanish trial (Table 4) chlorpyrifos residues were not detected (<0.01 mg/kg) in the pulp of mandarins when residues in the whole fruit were 0.14 mg/kg.

In laboratory-scale juicing of oranges treated at exaggerated application rates in the USA in 1977 and 1978 (Table 8) chlorpyrifos residues in the juice ranged up to 0.78 mg/kg with the median below the LOD (<0.01 mg/kg). Residues in the whole oranges were not measured.

Residues of chlorpyrifos were not detected (<0.01 mg/kg) in the juice of grapefruit, lemons, oranges or tangelos produced in simulated commercial processing (Table 9). Residues in the initial fruit were grapefruit 0.36 mg/kg, lemons 0.38 mg/kg, oranges 0.51 mg/kg, tangelos 0.59 mg/kg.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Chlorpyrifos residues were monitored in agricultural commodities in the California priority pesticide programme. The results for chlorpyrifos in citrus are shown in Table 10.

Table 10. Incidence of chlorpyrifos detections in citrus fruit in the California Department of Food and Agriculture Pesticide Program (Deukmejian and Voss 1990; Wilson *et al*., 1991, 1993).

Commodity	Number of samples			Year
	Analysed	Free of residues	Exceeding tolerance	
Grapefruit	11	11	0	1989
Lemon	5	5	0	1989
Orange (Navel)	58	35	0	1989
Lemon	2	2	0	1990
Grapefruit	27	27	0	1991
Mandarin	1	1	0	1991
Orange (Valencia)	9	6	0	1991

Estimates of the dietary intake of chlorpyrifos in the Australian diet were reported by Stenhouse (1992). Estimated daily intakes of chlorpyrifos for diets based on the average energy intake were: adult male 0.216 ì g/kg bw; adult female 0.272 ì g/kg bw; boy aged 12 0.292 ì g/kg bw; girl aged 12 0.314 ì g/kg bw; child aged 2 0.544 ì g/kg bw; infant aged 9 months 0.444 ì g/kg bw. These intakes should be compared with the current ADI for chlorpyrifos (10 ì g/kg bw).

Dejonckheere *et al*. (1993) estimated the dietary intake of chlorpyrifos in the Belgian diet arising from food commodities of plant origin. For a 60 kg person and using the average residue in food prepared for consumption the estimated intake was 0.074% of the ADI (10 ì g/kg bw).

Penttilä and Siivinen (1995) estimated the dietary intake of pesticide residues, including chlorpyrifos residues, in Finland. In 1992 the estimated chlorpyrifos intake from imported foods was 0.007 ì g/kg bw; chlorpyrifos is not registered in Finland for use in foodstuffs.

NATIONAL MAXIMUM RESIDUE LIMITS

The Meeting was aware that the following national MRLs for chlorpyrifos on citrus fruits had been established.

Country	MRL, mg/kg
Australia	0.5
Canada	1
European Union	0.3
Japan	0.3
South Africa	0.3
Spain	0.5
USA	1

APPRAISAL

The use of chlorpyrifos on citrus in the USA results in higher residue levels than the current CXL for citrus fruits, 0.3 mg/kg. The Meeting reviewed available information on analytical methods, frozen storage stability, use patterns, fate during processing and supervised trials on citrus in the USA, Spain and South Africa.

At the 21st Session of the CCPR in 1993 (ALINORM 93/24A para 251) chlorpyrifos was identified as a candidate for periodic review. It was listed for periodic review but not scheduled in the report of the 1995 CCPR (ALINORM 95/24A page 99, Annex 1 of Appendix IV). Information was available to the Meeting on physical properties and metabolism but these subjects are best reviewed in the context of the entire data base in the Periodic Review Programme.

In residue analytical methods chlorpyrifos was extracted from the substrate with acetone or methanol. The extract was cleaned up by hexane-acetonitrile partitions followed by passage through a small silica gel column. Chlorpyrifos residues were analysed by GLC with photometric detection of phosphorus. Limits of determination were 0.01 mg/kg and recoveries were generally good. The method was validated on citrus peel, pulp and juice and a number of other agricultural commodities and their processed fractions.

Chlorpyrifos residues were extracted from orange pulp and peel with dichloromethane in a method used in South African trials. Clean-up was effected by solvent partitioning and Florisil column chromatography, and residues were measured by GLC with an FPD. The LOD was 0.01 mg/kg.

An analytical method was also available for the metabolite 3,5,6-trichloro-2-pyridinol. Orange substrates were heated with methanolic sodium hydroxide before extraction to convert the chlorpyrifos residues to 3,5,6-trichloro-2-pyridinol. After clean-up and formation of the trimethylsilyl derivative the residue was determined by GLC with EC detection. The method measures the total residue, chlorpyrifos + 3,5,6-trichloro-2-pyridinol. When a duplicate sample is analysed for chlorpyrifos alone the level of 3,5,6-trichloro-2-pyridinol is estimated by difference. The LOD was 0.05 mg/kg. The method was validated for citrus and citrus fractions.

Information on the frozen storage stability of chlorpyrifos and 3,5,6-trichloro-2-pyridinol residues in an extensive range of raw agricultural and processed commodities was made available to the Meeting. Residues were generally stable (>70% remaining) under the test conditions (-18°C for 3 months and longer, some samples for 4 years).

Chlorpyrifos is registered in the USA for use on citrus fruits for the control of aphids, scale, mites, cutworms, grasshoppers, thrips, and other pests. A petroleum spray oil recommended for use on citrus trees may be added to dilute spray mixtures to improve control. Information on registered uses in South Africa and Spain was also provided.

In the USA chlorpyrifos may be applied to citrus orchards at 1.1-3.9 kg ai/ha with a 21-day PHI or at 3.4-6.7 kg ai/ha with a 35-day PHI. Residues in 11 US trials on oranges treated at maximum GAP rates were 0.098, 0.11, 0.26, 0.36, 0.38, 0.38, 0.39, 0.41, 0.49, 1.3 and 2.0 mg/kg. Residues on grapefruit in 4 trials where application was at 1.4 kg ai/ha and the fruit were harvested 21 days later were 0.05, 0.067, 0.31 and 0.34 mg/kg.

In South Africa the registered use allows chlorpyrifos to be applied to citrus orchards at a spray concentration of 0.0096-0.048 kg ai/hl with a PHI of 60 days. Residues in 5 South African trials on oranges according to this use pattern were 0.05, 0.12, 0.14, 0.19 and 0.21 mg/kg.

The registered chlorpyrifos use pattern on citrus in Spain allows a spray concentration of 0.075-0.10 kg ai/hl and a 21-day PHI. In 4 Spanish trials on mandarins according to this use pattern chlorpyrifos residues were 0.40, 0.55, 0.99 and 1.2 mg/kg.

The chlorpyrifos residues from the 24 trials on oranges, grapefruit and mandarins in rank order were 0.05, 0.05, 0.067, 0.098, 0.11, 0.12, 0.14, 0.19, 0.21, 0.26, 0.31, 0.34, 0.36, 0.38, 0.38, 0.39, 0.40, 0.41, 0.49, 0.55, 0.99, 1.2, 1.3 and 2.0 mg/kg. The Meeting estimated a maximum residue level of 2 mg/kg for chlorpyrifos on citrus fruits to replace the previous recommendation (0.3 mg/kg).

The pulp and peel of oranges were analysed separately in 10 South African supervised trials. In all samples, including those from trials where treatment was at exaggerated rates or harvest at intervals shorter than the official PHI, chlorpyrifos residues were not detected (<0.01 mg/kg) in the pulp. In a Spanish trial chlorpyrifos residues were not detected (<0.01 mg/kg) in the pulp of mandarins when residues in the whole fruit were 0.14 mg/kg.

Information was made available to the Meeting on the fate of field-incurred chlorpyrifos residues during the processing of oranges, grapefruit, lemons and tangelos.

In laboratory-scale extraction of juice from oranges treated at exaggerated application rates in the USA in 1977 and 1978, chlorpyrifos residues in the juice ranged up to 0.78 mg/kg with the median below the LOD (<0.01 mg/kg). Residues in the whole oranges were not measured.

Residues of chlorpyrifos were not detected (<0.01 mg/kg) in the juice of grapefruit, lemons, oranges and tangelos produced in simulated commercial processing. Residues in the initial fruit were 0.36 mg/kg in grapefruit, 0.38 mg/kg in lemons, 0.51 mg/kg in oranges, and 0.59 mg/kg in tangelos.

The Meeting concluded that chlorpyrifos levels in citrus pulp and juice produced from a crop treated with chlorpyrifos according to GAP were generally below the LOD (0.01 mg/kg).

Dietary intake studies in Australia, Belgium and Finland showed that the dietary intake of chlorpyrifos was much less than the current ADI.

RECOMMENDATIONS

The Meeting estimated the maximum residue level shown below, which is recommended for use as an MRL.

Definition of the residue: chlorpyrifos (fat-soluble)

Commodity		Recommended MRL, mg/kg		PHI on which based, days
CCN	Name	New	Previous	
FC 0001	Citrus fruits	2	0.3	21, 35

REFERENCES

Dejonckheere, W., Steurbaut, W., Drieghe, S., Verstraeten, R. and Braeckman, H. 1993. Pesticide residues in food commodities of vegetable origin and the total diet in Belgium 1991-1993. University of Gent, Belgium.

Deukmejian, G. and Voss, H.J. 1990. Residues in fresh produce - 1989. Pesticide Enforcement Branch, California Department of Food and Agriculture, USA.

Hollick, C.B. and Sandenskog, C. 1976. Determination of residues of chlorpyrifos (DOWCO 179) in oranges from South Africa treated with Dursban insecticide - cooperator Fisons. Laboratory report GHE-P-413. Dow Chemical Europe. Unpublished.

Hollick, C.B. and Walker, S. 1976. Determination of residues of chlorpyrifos (DOWCO 179) in oranges, from South Africa, following three applications of Dursban 4 insecticide. Cooperator Fisons. Laboratory report GHE-P-414. Dow Chemical Europe. Unpublished.

Khoshab, A., Berryman, T., Buendia, J., Molina, R., Gil, J.P. and Tordera, J. 1994. Residues of chlorpyrifos in whole mandarins at harvest following a single application of Dursban 4 (EF 747), Spain - 1993. Study R93-06. Report GHE-P-3733. DowElanco Europe. Unpublished.

Khoshab, A., Nicholson, A., Laurie, D. and Gil, J.P. 1993. Residues of chlorpyrifos and its pyridinol metabolite in whole mandarin fruit at intervals and in peel and pulp at harvest following a single application of Dursban 4 (EF 747) - Spain 1992. Study R92-12. Report GHE-P-3213. DowElanco Europe. Unpublished.

Penttilä, P.-L. and Siivinen, K. 1995. Control and intake of pesticide residues during 1981-1993 in Finland. National Food Administration, Finland.

Robb, C.K. 1991. Determination of chlorpyrifos residues in Valencia oranges. Project 89078. DowElanco USA. Unpublished.

Stenhouse, F. 1992. The 1992 Australian Market Basket Survey. National Food Authority. Australian Government Publishing Service, Canberra, Australia.

Wetters, J.H. 1973a. Determination of residues of O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate in sugar beets and solid fractions by gas chromatography. ACR 73.5. Dow Chemical USA. Unpublished.

Wetters, J.H. 1973b. Determination of residues of O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate in sugar beet liquid process fractions by gas chromatography. ACR 73.6. Dow Chemical USA. Unpublished.

Wetters, J.H. 1976. Determination of residues of O,O-diethyl O-(3,5,6-trichloro-2-pyridyl)phosphorothioate in sorghum green plant, silage, dry plant, and grain by gas chromatography. ACR 76.3. Dow Chemical USA. Unpublished.

Wetters, J.H. 1977. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in oranges, peel plus pulp, and juice following a foliar application with Lorsban insecticide. GH-C 1041. Dow Chemical USA. Unpublished.

Wetters, J.H. 1978. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in whole oranges, peels, pulp and juice following a foliar application with Lorsban insecticide. GH-C 1141. Dow Chemical USA. Unpublished.

Wetters, J.H. 1981. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol in whole citrus and citrus process fractions following foliar applications of Lorsban 4E insecticide. GH-C 1441. Dow Chemical USA. Unpublished.

Wetters, J.H. 1985. Residues of chlorpyrifos and 3,5,6-trichloro-2-pyridinol on or in whole oranges following a foliar application of Lorsban 4E insecticide with or without oil using high volume and low volume spray equipment. GH-C 1724. Dow Chemical USA. Unpublished.

Wetters, J.H. 1990. Summary of frozen storage stability studies for chlorpyrifos and 3,5,6-trichloro-2-pyridinol in various crops. Project GH-C 2308R. DowElanco, USA. Unpublished.

Wilson, P., Strock, J.M. and Wells, J.W. 1991. Residues in fresh produce - 1990. Pesticide Enforcement Branch, Department of Pesticide Regulation, California Environmental Protection Agency, USA.

Wilson, P., Strock, J.M. and Wells, J.W. 1993. Residues in fresh produce - 1991. Pesticide Enforcement Branch, Department of Pesticide Regulation, California Environmental Protection Agency, USA.

DITHIANON (180)

EXPLANATION

Dithianon was first evaluated in 1992. At the 1994 CCPR the delegation of Germany questioned the underlying database for the maximum residue level of 1 mg/kg on cherries proposed by the 1992 JMPR. The present Meeting received updated information on GAP, summaries of residue data for cherries and detailed comments by Germany (Anon., 1994a). The manufacturer provided data on two supervised residue trials in Germany (Weeren *et al*., 1994) and two in France (Carlon, 1992). A short summary giving information on GAP and on residues from supervised trials on apples was made available by Finland (Anon., 1994b). Information on GAP for pome fruits was provided by the UK (Anon., 1994c).

METHODS OF RESIDUE ANALYSIS

The cherry samples from the two new German trials were analysed for dithianon by the method of Specht (1994). A 50 g sample is homogenized with 30 ml water, 30 ml hydrochloric acid and 200 ml acetone. An aliquot of the extract is partitioned between water and acetone-hexane-dichloromethane. After the addition of 0.1 ml acetic acid the organic phase is brought to dryness and redissolved in 20 ml ethyl acetate/cyclohexane (1:1). A 5 ml-aliquot is cleaned up by gel permeation chromatography on Bio Beads S-X3 with cyclohexane/ethyl acetate (1:1) as eluent (eluate volume range 135-165 ml). After the addition of 0.1 ml acetic acid the eluate is evaporated to dryness and the residue is dissolved in dichloromethane/acetic acid (99.9:0.1) and cleaned up by silica gel column chromatography using the same solvent as eluent. The first 100 ml is discarded and chromatography is continued with a further 80 ml of the same eluent. The eluate containing 0.5 ml acetic acid is brought to dryness and the residue dissolved in 5 ml acetonitrile/acetic acid/methanol/water (46.8:0.2:8.0:45) for determination by HPLC with a UV detector (LOD 0.05 mg/kg).

In the trials on cherries conducted between 1967 and 1972 a colorimetric method (LOD between 0.03 and 0.06 mg/kg) was used (Sieper and Pies, 1968).

USE PATTERN

GAP for the world-wide use of dithianon was reported in the 1992 evaluation. The information on GAP provided to the present Meeting by Germany and the UK is basically the same as in 1992 but contains more details, e.g. in application rates (see Table 1). New information was provided only by Finland. German GAP for uses on cereals was requested in 1992. At present there is no authorization for uses on cereals in Germany; GAP for wheat is still pending.

Table 1. Registered uses of dithianon in Germany, Finland and the UK.

Crop	Country	Form.	Application			PHI, days
			Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Apple	UK	750 SC	1.3	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
	Finland	750 SC 500 SC		0.045	5	21
Crab-apple	UK	750 SC	0.83	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
Pear	UK	750 SC	1.3	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
Quince	UK	750 SC	0.83	0.05-0.075	8	28
		250 SC	0.3-0.5	0.06-0.1	10	28
Pome fruits	Germany	750 SC	0.56	0.038	12	21
Cherries	Australia			0.075-0.11	2-4	21
	Germany	750 SC	0.56	0.038	3	28
	Netherlands		0.49-0.78	0.049-0.052	4	28
	Switzerland			0.05-0.075	multiple	21
Strawberry	Finland	750 SC 250 SC			0.045	21
Wine grapes	Germany	750 SC	0.23-0.9	0.038-0.056	3-8	42
		250 WP	0.19-0.5	0.03	3-8	42
		333 SC	0.1-0.27	0.017-0.033	3-8	42
Hops	Germany	750 SC	0.38-1.5	0.038	10	14
		250 WP	0.25-1.0	0.025	12	14
		333 SC	0.17-0.67	0.017	10	14

RESIDUES RESULTING FROM SUPERVISED TRIALS

Cherries. In addition to the six German trials carried out in 1985/86 and evaluated in 1992, the Meeting received residue data from 1967 to 1972 on sour (7 trials) and sweet cherries (5 trials) in Germany. Two further trials on sour cherries which included residues in processed products were conducted in Germany in 1993. Two new trials on sweet cherries (1992) were also carried out in France. Details of the new and previously reported trials are given in Tables 2 and 3. The underlined residues are from treatments according to GAP.

Table 2. Residues of dithianon in sour cherries.

Country, Year	Application				PHI, days	Residues, mg/kg	Reference or report
	Form	No	kg ai/ha	kg ai/hl			
Germany,	253 SC	4	0.4	0.05	0	11	R 118-69/1
1967					3	9.8	
					9	7.9	
					16	6.3	
					23	2.9[1]	
					30	0.85	
					37	0.75	
1968	253 SC	4	0.4	0.05	0	9.6	R 118-69/2
					4	10	
					11	1.9	
					18	0.6	
					22	0.62[1]	
1969	253 SC	5	1.4	0.05	0	10	R 118-69/3
					2	6.9	
					7	7.7	
1971	253 SC	3	1.4	0.05	0	12	R 123-72/1
					7	6.4	
					14	6.8	
					21	4.3[1]	
					28	4.3	
1971	253 SC	3	0.75	0.05	0	13	R 123-72/2
					7	13	
					14	8.4	
					21	3.7[1]	
					28	1.6	
					35	0.89	
					42	1.0	
1972	253 SC	3	0.75	0.05	0	3	R 123-72/3
					2	2.6	
					4	1.9	

Country, Year	Application				PHI, days	Residues, mg/kg	Reference or report
	Form	No	kg ai/ha	kg ai/hl			
					7	1.4	
					14	0.62	
1972	253 SC	3	0.75	0.05	0	5.6	R 123-72/4
					2	5.2	
					4	3.7	
					8	2.9	
					14	1.5	
1985	750 SC	3	0.75	0.15	0	1.3	CME 02444
					13	0.66	
					20	0.17	
					27	0.2	
					34	0.14	
1985	750 SC	3	0.56	0.11	0	1.9	CME 02449
					14	1.3	
					21	0.8	
					28	0.41[2]	
1985	253 SC	3	1.0	0.2	0	0.86	CME 02443
					13	0.53	
					20	0.16	
					27	0.14	
					34	0.13	
1985	253 SC	3	0.76	0.15	0	2.6	CME 02445
					14	0.81	
					21	0.84	
					28	0.76	
					35	0.57	
Germany,	253 SC	3	0.59	0.15	0	2.5	CME 02223
1986					14	0.92	
					21	0.49	
					28	0.26[2]	
					35	0.2	
1986	750 SC	3	0.44	0.11	0	2.2	CME 02221
					14	0.86	
					21	0.28	
					28	0.22	
					35	0.12	

1993	750 SC	3	0.54	0.075	0	fruit 2.5	SKG-9303-01
			0.57		27	fruit 0.48[2]	15079
			0.56			fruit, washed 0.24	
						preserved <0.05	
						jam <0.05	
						juice <0.05	
1993	750 SC	3	0.56	0.075	0	fruit 3	SKG 9303-02
					27	fruit 0.77[2]	15080
						fruit, washed 0.28	
						preserved <0.05	
						jam <0.05	
						juice <0.05	
Netherlands, 1976		3	0.245		19	0.18	JMPR 1992 Evaluation
		3	0.245		21	2.0	

[1] according to Swiss GAP
[2] according to German GAP

Table 3. Residues of dithianon in sweet cherries.

Country, Year	Application				PHI, days	Residues, mg/kg	Reference or report
	Form	No	kg ai/ha	kg ai/hl			
Germany,	253 SC	10	0.4	0.05	0	4.5	R 118-69/4
1968					4	3.1	
					6	1.8	
					7	1.9	
1969	253 SC	6	0.4	0.05	0	6.9	R 118-69/5
					2	7.1	
					7	6.6	
1971	253 SC	3	1.6	0.05	0	7.4	R 123-72/5
					7	4.1	
					14	2.1	
					21	2.3[1]	
					28	1.4	
1971	253 SC	3	0.75	0.05	0	9.2	R 123-72/6
					7	7.6	
					14	3	
					21	1.9[1]	
					28	1.1	
Germany,	253 SC	3	0.75	0.05	0	6	R 123-72/7
1972					2	4.1	
					4	3.8	
					8	2.9	
					14	1.5	
France, 1992	750 SC	3	0.38	0.038	14	0.11	S/FR/R/92/072
1992	750 SC	3	0.38	0.038	28	0.05	S/FR/R/92/073

[1] According to Swiss GAP

Apples. Summary information on residues from supervised trials on apples was made available by Finland (Anon., 1994b). The trials (Table 4) do not reflect GAP in Finland: they may be considered only as supplementary to those reviewed in 1992 on which the maximum residue level estimated for pome fruit was based.

Table 4. Residues of dithianon in apples from supervised trials in Finland (Anon., 1994b).

dithianon

Year	Application				PHI, days	Residues, mg/kg
	Form	No	kg ai/ha	kg ai/hl		
1985	750 SC	4	2.0	0.045	34	0.03
		4	2.0	0.045	34	0.04
1986	750 SC	5	0.6	0.045	14	2.2[1]
		5	0.6	0.045	21	0.5[1]
		5	0.6	0.045	28	2.5[1]
1987	750 SC	5	0.6	0.045	21	16[1]
		5	0.6	0.045	28	12[1]
		5	0.6	0.045	35	9[1]
1988	750 SC	5	0.8	0.045	31	0.06
		5	0.8	0.045	32	0.2
		5	0.7	0.045	45	0.2
1989	750 SC	5	0.75	0.045	14	1.0[1]
		5	0.75	0.045	21	0.8[1]
		5	0.75	0.045	28	0.3[1]
1993	500 SC	5	0.5	0.045	14	1.1[1]
		5	0.5	0.045	21	1.1[1]
		5	0.5	0.045	28	0.9[1]

[1] Last spraying carried out about 30 days later than normal

APPRAISAL

Dithianon is a multi-site protective fungicide which inhibits spore germination. It was first reviewed by the 1992 JMPR. At the 1994 CCPR the delegation of Germany questioned the data on which the maximum residue level of 1 mg/kg on cherries estimated by the 1992 JMPR were based.

Items of further work or information listed as desirable by the 1992 JMPR were (1) additional studies on the fate of residues in farm animals (metabolism and transfer studies), and on plant metabolism and soil degradation, and (2) GAP and residue information for uses on cereals in Germany, The Netherlands and the UK.

The present Meeting received updated information on GAP, summaries of residue trials on cherries and explanatory notes by Germany. The manufacturer provided reports of two supervised residue trials from Germany and two from France. Summarized information on GAP was made available by Finland and the UK. A summary of residue trials on apples was also provided by Finland.

The determination of residues in cherries in older trials was by the formation of a coloured morpholine adduct. In the current procedure, cherries are homogenized with acetone, hydrochloric acid and water, the homogenate is partitioned with hexane and dichloromethane and the residue cleaned up by gel permeation chromatography with cyclohexane/ethyl acetate. After addition of 0.1 ml acetic acid the solvent is evaporated and the residue dissolved in acidified dichloromethane and cleaned up further by silica gel column chromatography. The determination is carried out by HPLC with UV detection. The LOD is 0.05 mg/kg.

The information on GAP provided by Germany and the UK is basically the same as supplied in 1992. Therefore at present there is no approved use on cereals in Germany or the UK.

The present Meeting reviewed the new reports of residue trials on cherries and apples in the context of those previously reviewed.

Cherries. The 1992 JMPR estimated a maximum residue level of 1 mg/kg, based on six German and two Dutch trials (3 treatments, 0.15-0.75 kg ai/ha) with residues from 0.14 mg/kg to 0.8 mg/kg at 21-28 days after treatment. The critical GAP exists in Australia (2-4 treatments, 0.075-0.113 kg ai/hl, 21-day PHI), and Switzerland (multiple applications, 0.05-0.075 kg ai/hl, 21-day PHI), followed by The Netherlands (4 treatments, 0.049-0.052 kg ai/hl, 0.49-0.78 kg ai/ha, 28-day PHI) and Germany (3 treatments, 0.038 kg ai/hl, 0.56 kg ai/ha, 28-day PHI).

In addition to the six German trials carried out in 1985/86 and evaluated in 1992, the Meeting received data on 7 trials on sour cherries and 5 trials on sweet cherries in Germany from 1967 to 1972, which could be evaluated on the basis of Swiss GAP. Diathianon was applied three to ten times at 0.05 kg ai/hl (0.4-1.4 kg ai/ha). After PHIs of 21-23 days the residues in the fruit ranged from 0.62 to 4.3 mg/kg.

In 1993 two further trials were conducted on sour cherries in Germany which included analyses of processed products. After three applications at 0.56 kg ai/ha and a 27-day PHI the residues in the fruit were 0.48 and 0.77 mg/kg, reduced by washing to 0.24 and 0.28 mg/kg respectively. No residues above the limit of determination (0.05 mg/kg) could be detected in preserves, jam or juice.

Two new trials on sweet cherries were carried out in France in 1992 (3 treatments, 0.38 kg ai/ha, 0.038 kg ai/hl). The residues 14 or 28 days after application were 0.11 and 0.05 mg/kg.

After re-evaluation of all results from application rates of 0.038-0.075 kg ai/hl or 0.49-0.78 kg ai/ha according to the reported European GAP the Meeting estimated a maximum residue level of 5 mg/kg for cherries to replace the previous recommendation (1 mg/kg).

Apples. A short summary repot of trials on apples was made available by Finland. Dithianon was applied four or five times a year at application rates from 0.5 to 2 kg ai/ha. Residues after a PHI of 21 days ranged from 0.5 to 16 mg/kg. The high residue occurred because the last treatment was carried out about 30 days later than usual. The data do not reflect GAP in Finland but may be considered as supplementing the results provided in 1992 on which an estimated maximum residue level for pome fruit was based. The Meeting considered that they supported the previous estimate of 5 mg/kg.

RECOMMENDATIONS

The Meeting estimated the revised maximum residue level for cherries shown below, which is recommended for use as an MRL.

Definition of the residue: dithianon

Commodity		Recommended MRL		PHI on which based, days
CCN	Name	New	Previous	
FS 0013	Cherries	5	1	21

FURTHER WORK OR INFORMATION

Desirable

Additional studies on the fate of residues in farm animals (metabolism and transfer studies), and on plant metabolism and soil degradation (from 1992).

REFERENCES

Anon. 1994a. Information on GAP, residue data and explanatory notes on dithianon for the 1995 JMPR. Federal Biological Research Centre for Agriculture and Forestry, Federal Republic of Germany, May 1994. Unpublished.

Anon. 1994b. Information on residues of dithianon in apples for the 1995 JMPR. Ministry of Trade and Industry, Advisory Committee on Foodstuffs, Finland, November 30, 1994. Unpublished.

Anon. 1994c. Information on GAP for dithianon for the 1995 JMPR. Pesticides Safety Directorate UK, November 31, 1994. Unpublished.

Carlon, R. 1992. Residues of dithianon in cherries from France treated with delan - 1992 trials. Betr. 93.006, budget code 876.72.700.

Sieper, H. and Pies, H. 1968. Verfahren zur Bestimmung des Fungizids Dithianon auf Äpfeln. Z. Anal. Chem. 242, 234-245.

Specht, W. 1994. HPLC- Bestimmung von Dithianon in pflanzlichem Material.
In: Determination of residues of dithianon in cherries and their processed products after application of SAG 107 11 F. SHELL trial No. SKG-9303-01 and SKG-9303-02, project identity SHE-9301 Az. 13932/93. Unpublished.

Weeren, R.D. Weber, H. and Kwasnick, A. 1994. Determination of residues of dithianon in cherries and their processed products after application of SAG 107 11 F. SHELL trial No. SKG-9303-01 and SKG-9303-02, project identity SHE-9301 Az. 13932/93. Unpublished.

DITHIOCARBAMATES (105)

APPRAISAL

Mancozeb, maneb and propineb were reviewed in the periodic review programme in 1993 and MRLs for dithiocarbamates were recommended.

Metiram, another dithiocarbamate, has now been evaluated by the present Meeting as a new compound, and the evaluation is elsewhere. The maximum residues arising from the use of metiram according to GAP do not exceed the current recommendations for dithiocarbamates, where these exist, but additional MRLs are needed for commodities that are not already covered.

The Meeting believed that it would be useful to have a consolidated list of the current recommendations that showed the compound(s) contributing to the recommendation for each commodity, and such a list is given in the Table of recommendations below.

The 1993 JMPR had estimated a maximum residue level of 2 mg/kg for dithiocarbamates on mangoes arising from the use of mancozeb (Report, p.85), but the entry had been inadvertently omitted from Annex I. The entry is included in the following Table as a JMPR recommendation.

The Meeting noted that there is a CXL for dithiocarbamate in endive, but no recommendation had been made during the 1993 periodic review of mancozeb, maneb and propineb. In the absence of adequate data the recommendation for an MRL should have been withdrawn. The recommendation to withdraw the CXL is now included in the following Table.

RECOMMENDATIONS

The maximum residue levels listed below are recommended for use as MRLs.

Definition of the residue: The MRLs refer to total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg.

Commodity		Recommended MRL, mg/kg	Compounds on which recommendations are based[1]			
CCN	Name					
AM 0660	Almond hulls	20		maneb		
TN 0660	Almonds	0.1*	mancozeb	maneb		
VS 0621	Asparagus	0.1	mancozeb			
FI 0327	Banana	2	mancozeb			
GC 0640	Barley	1	mancozeb			
AS 0640	Barley straw and fodder, dry	25	mancozeb	maneb		
VB 0041	Cabbages, Head	5	mancozeb	maneb		
VR 0577	Carrot	1	mancozeb			
VS 0624	Celery	Withdrawn[2]				
FS 0013	Cherries	Withdrawn[2]				

Commodity		Recommended MRL, mg/kg	Compounds on which recommendations are based[1]			
CCN	Name					
VP 0526	Common bean (pods and/or immature seeds)	1				metiram
VL 0510	Cos lettuce	10		maneb		
FB 0265	Cranberry	5	mancozeb			
VC 0424	Cucumber	2	mancozeb	maneb		
FB 0021	Currants, Black, Red, White	10	mancozeb			metiram
MO 0105	Edible offal (Mammalian)	0.1	mancozeb			metiram
PE 0112	Eggs	0.05*	mancozeb			
VL 0476	Endive	Withdrawn[4]				
VA 0381	Garlic	0.5	mancozeb			
FB 0269	Grapes	5	mancozeb	maneb	propineb	metiram
DH 1100	Hops, dry	30				metiram
VL 0480	Kale	15	mancozeb	maneb		
VA 0384	Leek	0.5	mancozeb			
VL 0482	Lettuce, Head	10	mancozeb	maneb		metiram
AS 0645	Maize fodder	2	mancozeb			
FC 0003	Mandarins	10	mancozeb			
FI 0345	Mango	2	mancozeb			
MM 0095	Meat	0.02*	mancozeb			metiram
VC 0046	Melons, except Watermelon	0.5	mancozeb		propineb	
ML 0106	Milks	0.05*	mancozeb			metiram
VA 0385	Onion, Bulb	0.5	mancozeb		propineb	
FC 0004	Oranges, Sweet, Sour	2	mancozeb			
FI 0350	Papaya	5	mancozeb			
FS 0247	Peach	Withdrawn[5]				
SO 0697	Peanut	0.1*	mancozeb			
AL 0697	Peanut fodder	5	mancozeb			
VO 0445	Peppers, Sweet	1	mancozeb	maneb		
FS 0014	Plums (including Prunes)	Withdrawn[2]				
FP 0009	Pome fruits	5	mancozeb		propineb	metiram
VR 0589	Potato	0.2	mancozeb	maneb	propineb	metiram
PO 0111	Poultry, Edible offal of	0.1	mancozeb			
PM 0110	Poultry meat	0.1	mancozeb			
VC 0429	Pumpkins	0.2	mancozeb			
VA 0389	Spring onion	10		maneb		
VC 0431	Squash, Summer	1	mancozeb			
FB 0275	Strawberry	Withdrawn[5]				
VR 0596	Sugar beet	0.5	mancozeb	maneb		
AV 0596	Sugar beet leaves or tops	20	mancozeb	maneb		
VO 0447	Sweet corn (corn-on-the-cob)	0.1*	mancozeb			
VO 0448	Tomato	5	mancozeb	maneb	propineb	metiram
VC 0432	Watermelon	1	mancozeb	maneb		
GC 0654	Wheat	1	mancozeb	maneb		metiram

Commodity		Recommended MRL, mg/kg	Compounds on which recommendations are based[1]			
CCN	Name					
AS 0654	Wheat straw and fodder, dry	25	<u>mancozeb</u>	maneb		metiram
VC 0433	Winter squash	0.1	<u>mancozeb</u>			

[1] The underlined compound(s) have principally determined the estimated maximum residue level
[2] 1993 recommendation
[3] 1995 recommendation
[4] 1995 recommendation, omitted in 1993 in error
[5] Withdrawal recommended by 1993 JMPR; withdrawn by 21st CAC

FENARIMOL (191)

IDENTITY

ISO common name: fenarimol

Chemical name

IUPAC: (±)-2,4′-dichloro-Æ-(pyrimidin-5-yl)benzhydryl alcohol

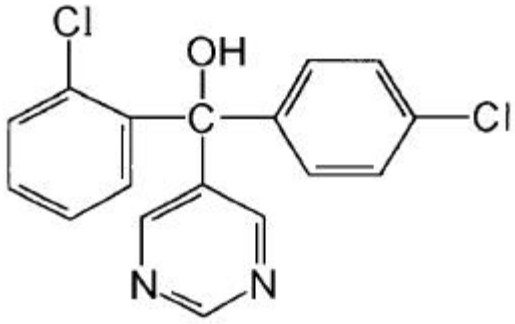
CA: (±)-Æ-(2-chlorophenyl)-Æ-(4-chlorophenyl)-5-pyrimidinemethanol

CAS registry no: 60168-88-9 (unstated stereochemistry)

CIPAC No: 380

Synonyms: compound 57322
development code EL-222

Structural formula:



Molecular formula: $C_{17}H_{12}Cl_2N_2O$

Molecular weight: 331.2

Physical and chemical properties

Pure active ingredient

Vapour pressure:	6.5×10^{-5} Pa at 25°C (99.7% pure) (A 21)	
Hydrolysis (no purity stated):	pH 3	no hydrolysis
(Dow Elanco Ltd., undated)	pH 6	no hydrolysis at 25, 37 and 52°C
	pH 9	no hydrolysis
Following 40 hours reflux at 100°C:	pH 3	30% hydrolysis
	pH 6	no hydrolysis
	pH 9	13% hydrolysis

Photolysis (no purity stated):

Sunlight or simulated sunlight

half-life in 2 mg/l water solution in summer sun: 12 hours
half-life in water in laboratory simulated sunlight: <1 hour
half-life on silica gel plates in sunlight: approx 14 hours (Day, undated)

Laboratory irradiation apparatus

half-life in distilled water: 0.6 hours
half-life in 2% acetone/water: 2.0 hours (Mosier and Saunders, 1976)

No information was submitted for the pure active ingredient on melting point, octanol/water partition coefficient, solubility or specific gravity.

Technical material

Purity:	Typically ≥97% with certified limits of 95-101% to allow for assay and production variability.
	Impurities <0.5%. except for the 2,2′-, 2,3′- and 4,4′-dichloro isomers of fenarimol (total max. 3%) (Day, 1985)
Colour:	off-white to buff (Day, 1984)
Physical state:	crystalline solid (Day, 1984)
Odour:	slightly aromatic (Day, 1984)
Melting point:	117-119°C (Day, 1984)
Octanol/water partition coefficient:	Log K_{ow} = 3.69 (Loh, 1976, Day, 1984)

Solubility
(mg/l at 25°C; purity was either 95.4% or unspecified)

water at pH 3	14.6
water at pH 7	13.7
water at pH 10	13.8
acetone	>250
acetonitrile	40-45
benzene	100-125
chloroform	>500
cyclohexanone	>500
ethyl cellosolve	>250
heavy aromatic naphtha	40-45
hexane	1.1
methanol	100-125
methyl cellosolve	>250
xylene	40-45 (Day, 1976, 1984)

Specific gravity:

Packed bulk density: 0.7 - 0.8 kg/m^3
Loose bulk density: 0.4 kg/m^3 (Hudson, 1987; Day, 1984)

Formulations

Fenarimol is formulated mainly as either WP, EC or SC products.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rats. [^{14}C]fenarimol was extensively metabolized in wistar rats with less than 3% of the dose excreted unchanged in the urine and faeces within 7 days, and with only trace amounts being detected in the bile. More than 40 metabolites, each representing only a small fraction (<10%) of the dose, were detected in the urine and faeces. Some 10 metabolites were tentatively identified by a combination of thin-layer chromatography/autoradiography, mass spectrometry, infrared spectrometry and nuclear magnetic resonance spectrometry. Many metabolites appeared to be common to both the urine and faeces. The proposed major metabolic pathways of fenarimol are oxidation of the carbinol-carbon atom, the chlorophenol rings and the pyrimidine ring, as shown in Figure 1. A proposed minor metabolic pathway involves cyclization between a chlorophenol ring and the pyrimidine ring (Goebel, 1985a; Althaus, 1985a).

Biliary metabolites existed predominantly as glucuronic acid conjugates, with similar metabolite profiles being seen at both the dose levels tested. The main metabolite present in bile after enzymatic hydrolysis was 4-[(2-chlorophenyl)(4-chlorophenyl)hydroxymethyl]-3-pyrazolone (metabolite K, Figure 1). In contrast, most of the radioactivity in the faeces was present as unconjugated compounds indicating that biliary metabolites undergo further metabolism or hydrolysis before being eliminated (Goebel, 1985a).

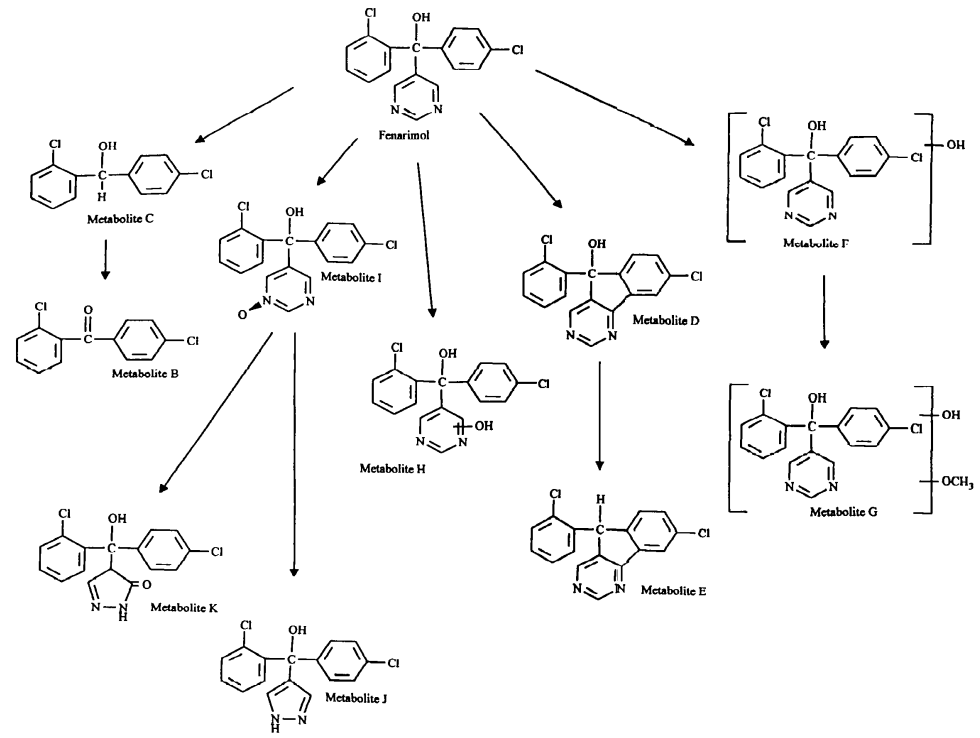
In a further study rats were dosed with a single oral dose of 1 or 13 mg/kg [^{14}C]fenarimol. The major radiolabelled constituents identified in the blood and kidneys 1 hour after dosing were unchanged fenarimol and fenarimol *N*-oxide (metabolite I); fenarimol predominated, except in the blood of low-dose males, as shown in Tables 1 and 2. Identification was by thin-layer chromatography. Fenarimol also accounted for most of the radioactivity in the liver 1 h after dosing (Table 3). In addition 3-6% of the radioactivity in the liver was tentatively identified as 4-[(2-chlorophenyl)(4-chlorophenyl)hydroxymethyl]-3-pyrazolone (metabolite K) (Althaus, 1985b).

Table 1. Major compounds in whole blood of male and female rats.

Blood	Dose, mg/kg	% of total ^{14}C	% of ^{14}C in blood		
			Fenarimol	Fenarimol *N*-oxide	Other
Male	1	0.152	19.3	41.3	39.4
Female	1	0.126	49.5	21.8	28.7
Male	13	1.154	40.4	36.7	22.9
Female	13	1.804	72.5	10.9	16.6

fenarimol

Figure 1. Proposed metabolic pathways of fenarimol in rats.



Metabolite Metabolite F: Three isomers observed. One isomer was hydroxylated in the 4-position of the 2-chlorophenyl ring and was confirmed by synthesis of the authentic model compound. The positions of the ring hydroxyl group in the other two isomers are unknown.

Metabolite G: This compound contains hydroxy and methoxy groups. Their positions are unknown.

Metabolite H: The position of the hydroxyl group on the pyrimidine ring is unknown.

Table 2. Major compounds in kidneys of male and female rats.

Kidneys	Dose, mg/kg	Fenarimol, %	Fenarimol *N*-oxide, %	Other, %
Male	1	48	19	32
Female	1	66	11	23
Male	13	64	15	21
Female	13	84	5	11

Table 3. Major compounds in liver of male and female rats.

Liver	Dose, mg/kg	Fenarimol, %	Metabolite K, %	Other, %
Male	1	67	6	27
Female	1	82	5	13
Male	13	77	6	17
Female	13	90	3	7

Goats. A lactating goat (breed unspecified) was dosed twice daily for 5 days with gelatine capsules containing [carbinol-^{14}C]fenarimol at a dose equivalent to 10 ppm in the diet and killed sixteen hours

after the final dose.

The radioactivity of tissue samples was determined by combustion/LSC. The chromatographic profiles of samples were determined by radio-TLC following preparation which generally involved an acidification and purification on a C18 column eluted with methanol. Flash chromatography was used to prepare some samples. Samples of protease-digested livers were also obtained. Further identification was carried out by HPLC with UV detection and/or GC-MS. Eighty two per cent of the total dose was excreted by the end of the study (urine 28%, faeces 53%, cage wash 0.7%, milk <0.1%). The tissues and gut contents accounted for 16% of the total dose. The maximum plasma concentration occurred 97 hours after the first dose (0.034 mg/l fenarimol equivalents) which coincided with the maximum concentration in whole blood (0.03 mg/l fenarimol equivalents) indicating that binding to red blood cells was not taking place. The maximum concentration in the milk occurred 80 hours after the first dose (0.08 mg/l fenarimol equivalents). The radioactivity in other compartments was distributed as shown in Table 4.

Table 4. Radioactivity in a goat dosed with [^{14}C]fenarimol.

Sample	mg/kg fenarimol equivalents	% of total dose
Bile	2.97	0.1
GI tract	0.18	0.82
GI tract contents	0.94	12.2
Carcase	0.02	2.0
Fat - omental	0.03	-
Fat - renal	0.03	-
Fat - subcutaneous	0.03	-
Kidneys	0.14	0.04
Liver	0.42	0.7
Muscle	0.01	0.1

At least 90% of the total radioactivity in muscle and fat samples was extractable. The compounds shown in Table 5 were identified.

Table 5. Extraction efficiency and metabolites detected in goats (% of radioactivity present).

Compounds[1]	Sample						
	Liver		Kidney		Faeces, %	Urine, %	Bile, %
	%[2]	mg/kg[3]	%	mg/kg			
Compound 1 + Compound 2	34	0.14	38	0.05	36	87	93
fenarimol	-		-		9	-	3
fenarimol + 2-chlorobenzoic acid	21	0.09	11	0.02	-	-	-
2-chlorobenzoic acid + 4-chlorobenzoic acid + dehydroxyfenarimol	-		-		9	--	
4-chlorobenzoic acid + dehydroxyfenarimol	-		4		-	-	-
Unidentified	40		43		42	0	3
Numer of unidentified compounds	4		3		3	0	1
Extractable ^{14}C as % of ^{14}C in sample	69		94		61	100	85

[1] See Figure 2
[2] Of extracted ^{14}C in sample
[3] Fenarimol equivalents

The presence of compounds 1 and 2 in liver, kidney and bile could not be confirmed with a second solvent system but was confirmed in faeces and urine.

Further characterization was attempted using protease-digested liver but no results were obtained owing to the low levels of radioactivity. GC-MS of the liver extract indicated the possible presence of a fenarimol methyl sulphone derivative (which may arise as a result of glutathione conjugation, thio-ether cleavage, methylation and oxidation) (McCorquodale & Prout, 1995).

Pigs. Three cross-bred pigs were dosed twice daily for 5 days by incorporation of labelled fenarimol (>99% radioch;emical purity) into the feed at a level of 1 ppm (dry matter). One pig was dosed with [*carbinol*-^{14}C], one with [2-*chlorophenyl*[^{14}C] and the third with [4-*chlorophenyl*-^{14}C]fenarimol. The animals were killed 6-7 hours after the final feed. The radioactivity of the samples was determined by combustion and/or LSC. Results are shown in Table 6.

Table 6. Total residues in pig tissues following dosing with [^{14}C]fenarimol (all label positions)

Sample	mg/kg fenarimol equivalents	LSC recovery from spiked samples (%)
Liver	0.19-0.24	106, 141
Kidney	0.05-0.06	114, 127
Fat	0.04-0.06	-
Muscle	0.01	105, 140

Liver samples were extracted with methanol and dichloromethane/sodium chloride solution and analysed by TLC with autoradiography following purification by column chromatography (silica gel eluted with toluene/ethyl acetate and methanol). Fat samples were extracted with "hexanes" and acetonitrile, and the ^{14}C measured by LSC. The distribution of radioactivity in various extracts was as shown in Table 7.

Table 7. Distribution of radioactivity in sample extracts.

Sample/fraction	Position of radiolabel/% of total ^{14}C in sample		
	carbinol	2-chlorophenyl	4-chlorophenyl
Liver			
unextracted	23	35	20
dichloromethane extract	65	57	68
aqueous extract	13	18	12
Fat			
acetonitrile extract	88	85	90
"hexanes" extract	12	14	10

The major compound in the dichloromethane extracts of liver and the acetonitrile extracts of fat was fenarimol, accounting for 41-43% of the total radioactivity in the liver and 90% of the total in the fat (Althaus *et al*., 1984).

Chickens. Eight chickens (Hubbard x White Mountain Cross) were fed for 5 days with a diet containing 0.7 or 7 ppm [*carbinol*-14C]fenarimol (radiochemical purity 99.8%) and killed within one hour of removing the feed. The radioactivity of the samples was determined by combustion and LSC, with the results shown in Table 8 (Athaus *et al*., 1982a).

Table 8. Radioactive residues in chicken tissues following dosing with [^{14}C]fenarimol.

Sample	Assay recovery (%)	mg/kg fenarimol equivalents	
		0.7 ppm diet	7 ppm diet
Liver	109	0.01-0.013	0.113-0.12
Kidney	126	0.005-0.006	0.06-0.07
Fat	91	0.001-0.002	0.02-0.05
Skin	90	0.001-0.002	0.02
Muscle	113	0.001	0.003-0.005

In a second study, six Leghorn hens were dosed for 7 days with a feed containing 0.6 ppm [*carbinol*-^{14}C]fenarimol (radiochemical purity >99%) and then for a further 23 days with untreated feed. Eggs were collected daily, bulked to form a composite sample and analysed by LSC. Assay recoveries were 86.0-98.6%. The highest level of radioactivity was detected in day 7 samples (0.003 mg/kg fenarimol equivalents). By day 10 (3 days after the final treated feed) the radioactivity had decreased to 0.001 mg/kg, and was equivalent to background levels by day 17 (10 days after withdrawing treated feed) (Althaus, 1982b).

Plant metabolism

Apples. [*Carbinol*-^{14}C]fenarimol (radiochemical purity >99%) was formulated as an emulsifiable concentrate and diluted to give a 40 mg/l aqueous emulsion. This was applied as a spray to apple trees (Jonathan). The location of the trials was unspecified. Applications were made to run-off (2-5 litres aqueous emulsion/tree/application) at 80% full bloom (unlabelled formulation), 80% petal fall and on nine other occasions (radiolabelled formulation) at one- to two-week intervals (equivalent to 80-200g ai/ha based on a planting density of 1000 trees/ha). The total radioactivity was determined by combustion/LSC. The distribution of radioactive residues is shown in Table 9.

Table 9. Distribution of radioactive residues in apples.

Time after spraying	Whole apple	Peel		Pulp	
	mg/kg fenarimol equivalents	% of ^{14}C in whole apple	mg/kg fenarimol equivalents	% of ^{14}C in whole apple	mg/kg fenarimol equivalents
6 hours	0.207	92	0.983	9	0.023
29 days	0.108	87	0.477	13	0.019
49 days	0.074	81	0.351	19	0.017

Samples were extracted with methanol/sodium chloride solution and dichloromethane, then analysed by TLC/LSC. The distribution of radioactivity in the extracts and the fenarimol content were as shown in Table 10.

Table 10. Distribution of radioactivity and fenarimol in apple extracts (mean of 2 trees).

Sample	% of ^{14}C in sample	[^{14}C]fenarimol in sample

fenarimol

	aqueous phase	dichloromethane extract	unextracted	% of total ^{14}C	mg/kg sample
6 hour peel	10.8	67.9	21.4	53	0.52
29 day peel	13.9	47.6	38.6	24	0.18
49 day peel	15.7	44.8	39.5	23	0.14
49 day pulp	57.7	32.5	9.9	18	0.003

The authors of the study state that radioactivity other than that from fenarimol, equivalent to 0.06 mg/kg fenarimol on a whole-apple basis in the 49-day peel samples, was "widely distributed between many compounds".

Samples of peel obtained 52 days after the final application were also taken to attempt to identify metabolites. The samples were refluxed with methanol/2N sodium hydroxide solution and then partitioned successively with dichloromethane and butanol. These extracts were analysed by LSC or purified by column chromatography (silica column eluted with methanol/water). Analysis was by TLC with detection by UV and/or autoradiography and comparison with photodegradation products. Following extraction, the radioactivity was distributed as shown in Table 11.

Table 11. Distribution of radioactive residues in peel fractions.

Fraction	% of peel radioactivity	mg/kg fenarimol equivalents
spent peel (after refluxing)	17.2	0.24
dichloromethane extract	50.9	0.70
butanol extract	26.4	0.36
aqueous phase	5.5	0.08

Several compounds were tentatively identified by comparison with photolysis products (photoproducts A, E, D and H, Figure 2), all at ≤1% of total radioactivity or ≤0.01 mg/kg fenarimol equivalents. The authors concluded that photochemical degradation occurred on the surface of the apple. Other compounds (including >40 which were very polar) were observed but not identified. They had similar chromatographic characteristics to photodegradation products (Althaus and Bewley, 1978a,b).

In a further study carried out in Chile radiolabelled fenarimol was formulated as emulsifiable concentrates, diluted to give 1000 mg/l aqueous emulsions and applied directly as a mist spray to apples (Starkrimson). Radiolabelling was either at the carbinol carbon or mixed carbinol and both chlorophenyl rings (radiochemical purity 99.5-99.9%).

Individual apples were sprayed with 1 ml of the formulation or to run-off (whichever occurred first). This rate is equivalent to 268 kg ai/ha based on an average yield of 30t/ha and a medium-sized apple weighing 112g. Samples were taken 14 days after application and separated into pulp and peel.

Peel samples were extracted with aqueous methanol and dichloromethane, then refluxed with 2-butanol/water before partitioning between dichloromethane and aqueous methanol. Analysis was by TLC with autoradiography and LSC. The distribution of radioactive residues was as shown in Table 12.

Table 12. Distribution of radioactive residues in apple peel extracts.

Sample	[^{14}C]carbinol		mixed label ^{14}C	
	% of radioactivity	mg/kg fenarimol equivalents	% of radioactivity	mg/kg fenarimol equivalents
First dichloromethane	84	3.4	86	4.2
First aqueous	3	0.1	5	0.24
Second dichloromethane	3	0.1	3	0.15
Second aqueous	1	0.04	1	0.05
Unextractable	9	0.4	5	0.24
Total	100	4.0	100	4.9

Pulp samples were found to contain *c.* 0.06 mg/kg fenarimol equivalents in both experiments. TLC and LSC of peel samples identified *c.* 65% of the ^{14}C from both labels as the parent (*c.* 3 mg/kg).

No differences were detected between the TLC autoradiographs from the two radiolabels. No major degradation product was detected. Individual degradation products accounted for 2% of the total radioactivity, and all those identified in the peel were present as photolysis products. Small amounts of the major photolysis product *o*-chlorobenzoic acid were detected (Althaus, 1984a).

Grapes. A mixture of [*carbinol*-^{14}C], [*4-chlorophenyl*-^{14}C] and [*2-chlorophenyl*-^{14}C]fenarimol was formulated as an emulsifiable concentrate and diluted to give 120 mg/l and 500 mg/l aqueous emulsions. These were applied as foliar sprays to grapes (Ribier) four times at two-week intervals (120 mg/l formulation; total dose equivalent to 0.166 kg ai/ha) or once (500 mg/l formulation; dose unspecified). Samples were collected 0, 15, 30, 45 and 60 days after the final treatment.

Samples from the multiple-treatment study were extracted with methanol and partitioned with dichoromethane. The spent grape residue was extracted with 2-butanol-water by Soxhlet. The distribution of radioactivity was as shown in Tables 13 and 14.

Tables 13 and 14. Distribution of radioactivity in grapes following multiple applications of [^{14}C]fenarimol.

Table 13.

Days after final application	Total radioactivity as mg/kg fenarimol	% of total radioactivity			
		Dichloromethane	Aqueous	Butanol	Remainder
0	0.66	67.5	l6.8	8.5	7.2
15	0.46	63.6	15.2	11.7	9.5
30	0.33	61.6	16.1	8.1	14.3
45	0.33	59.8	16.8	9.0	14.4
60	0.19	56.4	18.2	11.1	14.3

Table 14.

Days after final application	TLC of dichloromethane fraction					
	Fenarimol		"Metabolite complex"		Unidentified	
	%[1]	mg/kg	%[1]	mg/kg[2]	%[1]	mg/kg[2]
0	46.0	0.305	12.7	0.08	8.8	0.06
15	26.9	0.124	26.5	0.12	10.2	0.05
30	19.3	0.063	29.1	0.10	13.2	0.04
45	17.8	0.058	27.9	0.09	14.1	0.05
60	15.6	0.029	26.5	0.05	14.3	0.03

[1] Of total radioactivity in Table 13
[2] Fenarimol equivalents

Samples taken 60 days after the single application were extracted into acidic water, refluxed with neutral, basic or acidic aqueous methanol, combined with sodium chloride solution, partitioned with dichloromethane, and then further partitioned with neutral, basic or acidic dichloromethane.

Neutral and acidic dichloromethane extracted 61 and 67% of the total radioactivity respectively. The extracts contained fenarimol and "metabolite complex" (which was not identical in different extracts). The term "metabolite complex" was applied to a group of two major, one minor and several trace components which were "extractable in the non-polar organic solvents , but which possessed polar adsorption chromatographic properties."

After extraction under strongly basic conditions the dichloromethane phase contained 74% of the total radioactivity but did not contain significant amounts of "metabolite complex".

Three compounds were identified: fenarimol (20%), dehydroxyfenarimol (DHF, 22%) and 2,4′-dichlorobenzophenone (DCBP, 8%). The structures of these compounds are shown in Figure 2 below. The "metabolite complex" was thermally degraded when subjected to GLC or MS, degraded by aqueous hydrolysis, and bound strongly during HPLC (Althaus, 1984b).

Further studies were conducted to identify the components of the "metabolite complex". Grape samples were refluxed with methanol/water, the extract was diluted with aqeous NaCl solution and extracted with dichloromethane. After drying, the residue was reconstituted in aqueous methanol and sequentially partitioned with hexane, chloroform/trichloroethane, and dichloromethane. The distribution of radioactivity was as shown in Table 15.

Table 15. Composition of grape extracts after sequential partitioning.

Solvent	% of radioactivity extracted as				
	Fenarimol	"Metabolite complex"[1]			Total
		Zone A	Zone B	Zone C	
Hexane	1-2	0	0	0	2
80:20 Chloroform/trichloroethane	18	3	1	1	27
50:50 Chloroform/trichloroethane	0.5	6	3	2	15
Dichloromethane	<0.5	1	5	2	9
Total	*c.* 20	10	9	5	53

[1] Zones refer to retention on TLC plate. Zone C most polar, Zone A least polar.

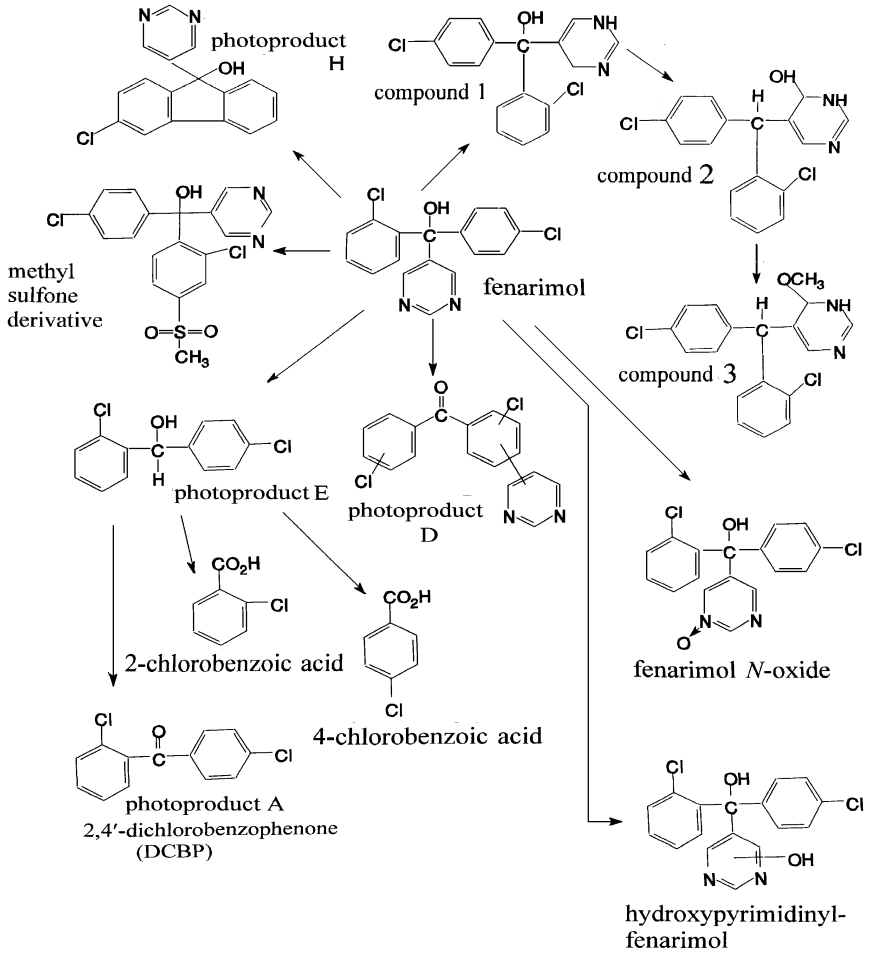
The 50:50 chloroform/trichloroethane and the dichloromethane fractions were subjected to further aqueous/methanolic sodium hydroxide hydrolysis when *c.* 50% of the extracted radioactivity was attributed to dehydroxyfenarimol (DHF) and 2,4′-dichlorobenzophenone (DCBP). The dehydroxyfenarimol was apparently produced during the hydrolysis.

Further analytical investigations of the "metabolite complex" in the basic extract were carried out using radio-HPLC, NMR and MS.

Compound 3 (Figure 2) was tentatively identified by MS but could not be confirmed by NMR, owing to the small quantity obtained. Compound 1 was tentatively identified by MS. Positions of reduction of the pyrimidine ring were investigated using NMR. Compound 2 was tentatively identified by MS but there was too little for confirmation by NMR. Three isomeric structures could exist (where -H and -OH have been added to the pyrimidine ring). The hypothesis that compound 1 could be converted to compound 2 under acidic conditions and subsequently to compound 3 by methanolysis under acidic conditions was proposed.

fenarimol

Figure 2. Proposed pathways of metabolism in livestock and plants, and of potodegradation.



In further work to characterize other metabolites in grapes, it was concluded that the unidentified radioactivity was associated with many minor components (34 "zones" were isolated). No individual component accounted for more than 2.9% of the total radioactivity (0.04 mg/kg fenarimol equivalents) (Goebel, 1985b; Rainey, 1987).

Cucumbers. [*Carbinol*-^{14}C]fenarimol was formulated as an emulsifiable concentrate and diluted to give a 26.5 mg/l aqueous emulsion. It was applied as a spray to field-grown cucumbers (Green Prolific) in the USA. One application was made to run-off at a rate equivalent to 24.7g [^{14}C]fenarimol in 934 litres water/ha. Samples were taken four days after treatment and analysed by combustion and/or LSC. The characterization of metabolites was carried out by radio-TLC.

After extraction by refluxing with methanol and further extraction with dichloromethane the total radioactivity in the crop ranged from 0.003 to 0.042 mg/kg fenarimol equivalents. Approximately 93% of this (0.04 mg/kg fenarimol equivalents) was extracted into dichloromethane and 85% of the extracted radioactivity (0.03 mg/kg fenarimol equivalents) was attributed to fenarimol and 8% (0.003

mg/kg fenarimol equivalents) remained at the origin. Three other chromatographic bands were separated, each accounting for 3% of the radioactivity (0.001 mg/kg fenarimol equivalents) (Althaus, 1986).

Environmental fate in soil and water/sediment systems

No data were submitted.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods for the analysis of a wide range of samples were supplied. In all of these the final determination is by GLC of a toluene solution, with EC detection. Validation data are shown in Table 16.

Crops and soil. Samples were extracted with ethanol/acetone, partitioned into chloroform, dissolved in toluene and analysed by GLC with an ECD. No validation data were submitted (Dow Elanco Ltd., 1976).

Crops other than cereals. Samples were extracted with methanol, partitioned into dichloromethane and transferred to toluene for analysis. No validation data were submitted (Dow Elanco Ltd., 1977).

Fresh fruit and vegetables, pomace, raisins, juice, bananas and "other crops". Samples were extracted with methanol, methanol/water or dichloromethane, then purified by chromatography on an alumina column which was eluted with 1-chlorobutane/methanol. The extract was evaporated and the residue dissolved in toluene for analysis. The authors state that the procedure "usually gives recoveries in excess of 90%" and has a limit of detection of 0.02 mg/kg except in dry pomace and "other crops" where the limit of detection is 0.01 mg/kg. No other validation data were submitted (Griggs and Decker, 1981).

Animal feeding-stuffs (hay and straw). Samples were extracted with methanol/water then purified by chromatography on an alumina column, which was eluted with 1-chlorobutane/methanol, before transfer to toluene (Griggs and Decker, 1985).

Beer. Samples were combined with sodium hydrogen carbonate solution, and partitioned into toluene for analysis (Butcher, 1992).

Spent yeast. Samples were extracted with methanol and, after dilution with water, partitioned with toluene. The extract was concentrated to dryness and the residue dissolved in 30:70 acetonitrile/water, then cleaned up on a C18 column eluted with 50:50 acetonitrile/water, acidified and partitioned into toluene (Butcher, 1992).

Fresh, dried and spent hops. Samples were extracted with methanol and sodium hydrogen carbonate solution and partitioned into methyl isobutyl ether. The extract was treated with alkaline permanganate, partitioned into toluene, dissolved in 1-chlorobutane, and cleaned up on an alumina column eluted with methanol/1-chlorobutane and on a C18 column eluted with acetonitrile/water. After acidification, the extract was partitioned into toluene for analysis (Butcher and Perkins, 1992).

Grape must, wine, grapes, tomatoes, peaches and melons. Samples were extracted with methanol and sodium hydrogen carbonate solution, partitioned into toluene, transferred to dichloromethane and

cleaned up on a C18 column eluted with methanol/dichloromethane or on a silica extraction column eluted with methanol/dichloromethane. The solvent was evaporated and the residue dissolved in toluene for analysis by capillary GLC (Butcher and Long, 1993; Butcher, 1994a).

Soil. Samples were extracted with methanol/water and cleaned up by column chromatography on alumina. Elution was with 1-chlorobutane/methanol. The authors state that the procedure "usually gives recoveries in excess of 90%" and has a limit of detection of 0.02 mg/kg. No other validation data were submitted (Griggs and Decker, 1981,1985).

Banana and banana pulp. Samples were ground with liquid nitrogen, then refluxed in methanol/HCl. NaOH was added to the hot solution which was then allowed to cool. The extract was partitioned with hexane and the hexane fraction washed through sodium sulphate, then evaporated to dryness. The residue was redissolved in toluene and analysed on a 2% OV 17 column. The compounds I and II (Figure 2) are also be determined by this method as dehydroxyfenarimol (Turner, 1992).

In a development of this method the methanol from the reflux solution was evaporated after the addition of NaOH. The remaining aqueous solution was extracted with dichloromethane, which was evaporated and the residue reconstituted in aqueous sodium chloride solution and partitioned with diethyl ether. The ether was evaporated and toluene added. The toluene extract was cleaned up on a silica solid-phase extraction column with elution with 10% ethyl acetate in dichloromethane. After evaporation the reconstituted toluene extract was analysed as above (Catta-Preta and Matos, 1993).

Wildlife. Meat and egg samples were extracted with methanol/acetonitrile or methanol and methylene chloride. Fat was extracted with hexane/1-chlorobutane and milk with acetonitrile, which was washed with hexane and partitioned with methylene chloride. Extracts were cleaned up on a Florisil column, eluted with methylene chloride/methanol, and dissolved in toluene (Yordy and Turner, 1982).

Table 16. Validation of analytical methods (treated plants, plant products, foodstuffs and feeding-stuffs).

Substrate	Spike, mg/kg % recovery	Precision-repeatability	Limit of determination, mg/kg	Reference
Whole apple fruit	0.001-0.02 73-98	no data	0.002-0.003	OR 1B
Dried apple pomace	0.005-0.1 65-103	no data	0.01	OR 1B
Whole fresh grapes	0.001-0.02 100-110	SD + 1-10	0.002-0.003	OR 1B
Wine	0.001-0.02 101-123	SD $\pm$ 2-14	0.002-0.003	OR 1B
Wine	0.01-0.1 99-107	RSD 2.5%	0.01	OR 22
Beer	0.01-0.1 90-108	RSD 4.0%	0.01	OR 21
Spent yeast	0.01-0.1 77-105	RSD 9.7%	0.01	OR 21
Dried hops	0.1-5 78-108	RSD 10.1%	0.1	OR 20
Fresh hops	0.1-2 75-94	RSD 7.4%	0.05	OR 20
Spent hops	0.02-0.5 75-102	RSD 8.3%	0.02	OR 20

Substrate	Spike, mg/kg % recovery	Precision-repeatability	Limit of determination, mg/kg	Reference
Tomatoes	0.01-0.1 86-101	RSD 5.1%	0.01	OR 24
Peach flesh	0.01-0.1 82-117	RSD 9.3%	0.01	OR 24
Melon peel	0.01-0.1 93-109	RSD 5.0%	0.01	OR 24
Melon pulp	0.01-0.1 81-112	RSD 10.2%	0.01	OR 24
Meat	0.01 101	SD ± 16.5	0.01	OR 19
Liver	0.01 108	SD ± 11.5	0.01	OR 19
Kidney	0.01 105	SD ± 13.7	0.01	OR 19
Fat/skin	0.01 87	SD ± 9.1	0.01	OR 19
Milk	0.001 95	SD ± 16.4	0.01	OR 19
Eggs	0.01 98	SD ± 9.0	0.01	OR 19
Banana	0.005-1.0 84-114	no data	0.01	OR 27
Banana pulp	0.005-1.0 82-105	no data	0.01	OR 27
Banana	0 005-1.1 55-114	no data	0.01	OR 28
Banana pulp	0.01-0.53 54-110	no data	0.01	OR 28

Stability of pesticide residues in stored analytical samples

Samples of grapes and wine were fortified with 0.1 mg/kg or mg/l fenarimol and stored deep frozen at -10°C to -27°C up to 370 days. Residues following storage and corrected for procedural recoveries were as shown in Table 17 (Butcher, 1994b).

Table 17. Residues in grapes and wine following storage at -20°C.

Storage period (days)	Residues, mg/kg			
	Black grapes	White grapes	Red wine	White wine
0	0.10-0.11	0.10-0.11	0.09-0.10	0.10
86	0.10-0.11	0.10-0.11	0.10-0.11	0.10
370	0.09-0.10	0.09-0.10	0.09-0.10	0.08-0.11

Ground fresh grapes and grape pomace were fortified with fenarimol at 0.05 mg/kg, and ground raisins and raisin waste at 0.2 mg/kg. Following 14 days refrigeration at 4°C, the samples were stored frozen for an additional 50-119 days. Samples were analysed after 0, 1, and 14 days and at the end of the study. Residues following storage and corrected for procedural recoveries were as shown in Table

18 (Day and Saunders, 1988a).

Table 18. Residues in fresh grapes, wet pomace, raisins and raisin waste following refrigeration and freezer storage.

Storage period, days	Residues, mg/kg			
	Fresh grapes	Wet pomace	Raisins	Raisin waste
0	0.054	0.054	0.20	0.19
1	0.052	0.055	0.18	0.23
14	-	0.049	0.18	0.17
18/19	-	-	0.19	0.21
23	0.050	-	-	-
74/76	-	-	0.19	0.18
131/133	0.052	0.054	-	-

In a further study, samples of cherries were fortified with 0.1 or 1.0 mg/kg fenarimol and stored for 11 days in a chill room at 4°C, then for 93 days in the freezer at -20°C. Samples were analysed using the method of Griggs and Decker (1981). Recoveries were variable but acceptable. The results, corrected for procedural recoveries, were as shown in Table 19 (Day and Saunders, 1988b).

Table 19. Residues in cherries following storage at -20°C.

Fortification level, mg/kg	Residue, mg/kg			
	Sweet cherry		Sour cherry	
	0.1	1.0	0.1	1.0
Storage period (days)				
0	0.11, 0.11	1.1, 1.1	0.11, 0.11	1.1, 1.1
4	0.09, 0.11	1.1, 1.1	0.10, 0.11	1.1
7	0.12, 0.13	1.1, 1.10	0.13, 0.11	1.1, 1.2
11	0.12, 0.13	1.2, 1.3	0.15, 0.13	1.3, 1.3
30	0.10, 0.10	0.9, 1.0	0.11, 0.10	1.0, 1.0
68	0.10, 0.10	0.9	0.11, 0.10	0.93, 0.91
104	0.11, 0.11	1.1, 1.0	0.10, 0.10	1.2, 1.1

A new study on the stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditions was made available, but too late for review (Butcher, 1995g).

Residue definition

The animal and plant metabolism studies indicate that fenarimol is the major residue in products of both animal and plant origin. The residue is therefore defined as fenarimol.

USE PATTERN

Fenarimol is a systemic fungicide which has protective, curative and eradicative activity. Most commonly it is applied as a foliar treatment where apoplastic movement occurs through the leaf and towards the leaf tip, but movement from treated to untreated leaves is not sufficient to provide disease control. Application via the roots and seeds leads to translocation to all the aerial parts of the plant.

Fenarimol is registered in a large number of countries. Its uses cover a wide range of fruit and vegetables, hops and wheat. Full details of registered use patterns are given in Tables 20-22. The registered uses are for treatments in the field unless otherwise indicated.

Table 20. Registered uses of fenarimol on fruits and pecans.

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Apples	Australia	EC	airblast	0.043-0.054	0.0029-0.0036	1-10	14	1 & 2
	Argentina	EC	mist blower broadcast	0.048-0.09	0.0024-0.003	2	20	1

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Belgium	WP	LV overall	0.03-0.06	-------	3-4	1 month	1
	Brazil	EC	mist blower broadcast	0.038-0.14	0.0048-0.0072	2	28	1
	Chile	EC	Gun broadcast med vol	0.038-0.096	0.0036-0.0042	2	(a)	1
	Denmark	EC	HV overall	0.060	0.006-0.004	5	14	1 & 11
	Germany (Rubigan EC)	EC	L/HV row	0.0108-0.054	0.0036	max 7	21	1 & 8
	Germany (Elital)	SC	L/HV overall	0.0108-0.054	0.0036	max 14	21	1 & 8
	Germany (Rubigan SC)	SC	L/HV row	0.0108-0.054	0.0036	max 14	21	1 & 8
	Greece	WP	HV overall	0.105	0.0042	3-5	20	1
	Ireland	SC	LV overall	0.04-0.08	-------	up to 14 usually 4-6	14	1
	Italy	EC	HV overall	0.054-0.072	0.0036-0.0048	Through-out season	21	1
	Italy	SC	HV overall	0.054-0.072	0.0036-0.0048	Through-out season	21	1
	Italy	WP	HV overall	0.054-0.072	0.0036-0.0048	Through-out season	21	1
	Japan	WP	airblast	0.09-~0.14	0.003-~0.004	1-3	21	1
	Mexico	EC	mist blower	0.054-0.108	0.0027-0.0036	2	(b)	1
	Netherlands[1] (country submission)	WP	spraying of the aerial part	0.039-0.076	0.0039-0.076	3	21	6
	Netherlands (company submission)	WP	HV overall	0.039-0.076	0.0026-0.076	max 10	3 weeks	1
	New Zealand	SC	HV to run-off	0.0067-0.090	0.003	6	35	5
	Peru[1] (country submission)	-	foliar application	-	0.05	3	30	7
	Peru (company submission)	EC	gun broadcast	0.012-0.060	0.0015-0.004	2	(a)	1
	Portugal	EC	HV overall	0.024-0.054	0.0024-0.0036	5	21	1
	Spain	EC	low volume spray (500-1,500 l/ha)	-	0.0042-0.0048	7-10 days intervals	14	4
	Spain	EC	high volume spray (>1,500 l/ha)	0.060-0.096	-	7-10 days intervals	14	4
	Spain	SC	HV overall	0.063-0.072	0.0042-0.0048	1	14	1
	UK	SC	LV overall	0.04-0.08	-------	up to 14 usually 4-6	14	1
	Uruguay	EC	broadcast mist blower	0.075-0.090	0.0024-0.003	2	20	1
	USA	SC	spray	0.049-0.098	-	7-14***	30	4
	USA	EC	spray	0.067-0.101	-	7-10***	30	4

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Bananas	Honduras[1]	EC	Aerial	0.08-0.12	0.0053-0.006	7	0 (c)	1
	Nicaragua[1]	EC	Aerial	0.08-0.12	0.533-0.6	7	0 (c)	1
Currants								
, black	Denmark	EC	HV overall	0.06	--------	3	14	1
, black	Ireland	SC	LV overall	0.04	--------	NR	14	1
	Netherlands[1] (country submission)	EC	spray	0.048-0.058	0.0048	4	21	6
	Netherlands (company submission)	EC	HV overall	0.048-0.058	0.0048	5	3 weeks	1
, black	UK	SC	LV overall	0.04	--------	NR	14	1
Cherry	Denmark	EC	HV overall	0.060	--------	5	14	1
	Japan	WP	airblast	0.16 ~0.2	0.004	1-3	3	1
	USA	EC	spray	0.051-0.101	-	4-8***	up to & after harvest	4
Gooseberries	Ireland	SC	HV overall	0.04	-------	NR	14	1
	Netherlands	EC	spray	0.048-0.058	0.0048	4	21	1
	UK	SC	HV overall	0.04	-------	NR	14	1
Grapes	Argentina	EC	gun individual plant	0.0192-0.036	0.0024	2	30	1
	Australia	EC	airblast	0.012-0.024	0.0012-0.0024	1-7	14	1
	Brazil	EC	gun individual plant	0.0108-0.024	0.0018-0.0024	4	15	1
, table	Chile	EC	gun individual plant	0.005 0.012	0.002-0.003	3	(d)	1
	France	SC	LV overall	0.018	0.0009-0.003	1 to 4	7	1
, wine	Germany[1] (Elital) (country submission)	SC	spray	0.0047-0.0125	0.00078	6	35	8
	Germany (Elital) (company submission)	SC	L/HV overall	0.0047-0.0234	0.00156	max 6*	35	1
	Germany (Rubigan SC)	SC	L/HV row	0.0047-0.0234	0.00156	max 6	35	1
	Greece	WP	HV overall	0.012-0.024	0.0012-0.0024	2-4	30	1
	Ireland	SC	LV overall	0.04	-------	NR	14	1
,table	Italy	WP	HV overall	0.03-0.06			14	1
,table	Italy	SC	HV overall	0.018-0.036	0.0018-0.0036	--------	14	1
, wine	Italy	SC	HV overall	0.014-0.054	0.0018-0.0036	--------	14	1
, wine	Italy	WP	HV overall	0.014-0.036	0.0018-0.0036		14	1
	Mexico	EC	mist blower	0.030-0.054	0.0075-0.0054	4	(e)	1
	New Zealand	SC	HV spray to run-off	0.024-0.048	0.0024	4	30	5
	Peru[1] (country	-	foliar	-	0.02	4	30	7

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	submission)		application					
	Peru (company submission)	EC	gun broadcast	0.012-0.060	0.0012-0.005	3	(d)	1
	Portugal	EC	HV overall	0.011-0.03	0.0018-0.0030	3	7	1
	Spain	EC	MV-HV overall	0.0099-0.05	0.0033-0.0036	1 (wine) 3(table)	28 (wine) 14 (table)	1
	Spain	SC	MV-HV overall	0.009-0.05	0.003-0.0036	1 (wine) 3(table)	28 (wine) 14 (table)	1
	UK	SC	spray	0.04	-------	NR	14	1 & 4
	Uruguay	EC	gun application individual plant	0.019-0.036	0.0024	2	30	1
	USA	EC	spray	0.017-0.051	_	3-9***	30	4
	USA	SC	spray	0.024-0.049	-	2-7***	30	4
Peaches	Argentina	EC	mist blower	0.048-0.072	0.0024	2	20	1
	Greece	WP	HV overall	0.12	0.0048	2-4	20	1
	Italy	EC	HV overall	0.072	0.0042-0.0048	2-3	14	1 & 12
	Italy	SC	HV overall	0.072	0.0042-0.0048	2-3	14	1 & 12
	Japan	WP	airblast	0.12-~0.2	0.004	1-3	1	1
	Spain	EC	HV overall	-	0.0042-0.0048	1	7	4
	Spain	SC	HV overall	-	0.0042-0.0048	1	7	4
	Uruguay	EC	broadcast mist blower	0.048-0.072	0.0024	2	20	1
Pears	Argentina	EC	mist blower broadcast	0.048-0.09	0.0024-0.003	2	20	1
	Australia	EC	airblast	0.043-0.054	0.029-0.0036	1-10	14	1 & 2
, Japanese	Australia	EC	airblast	0.036-0.054	0.0024-0.0036	1-10	14	1 & 2
	Belgium	WP	LV overall	0.03-0.06	--------	3-4	1 month	1
	Chile	EC	Gun broadcast med. vol	0.038-0.096	0.0036 0.0042	2	(a)	1
	Denmark	EC	HV overall	0.060	--------	5	14	1
	Germany (Elital)	SC	L/HV overall	0.0108-0.054	0.0036	max 14	21	1 & 8
	Italy	EC	HV overall	--------	0.0036-0.0048	**	14	1
	Italy	SC	HV overall	--------	0.0036-0.0048	**	14	1
	Italy	WP	HV overall	0.054-0.072	0.0036-0.0048	**	14	1

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Japan	WP	airblast	0.09-~0.12	0.003-~0.004	1-3	21	1
	Mexico	EC	mist blower	0.054-0.108	0.0027-0.0036	2	(b)	1
	Netherlands[1] (country submission)	WP	spraying of the aerial part	0.039-0.076	0.0039-0.076	3	21	6
	Netherlands (company submission)	WP	HV overall	0.039-0.076	0.0026-0.0076	max 10	3 weeks	1
	New Zealand	SC	HV to run-off	0.0067-0.090	0.003	6	35	5
	Portugal	EC	HV overall	0.024-0.054	0.0024-0.0036	5	21	1
	Spain	EC	HV overall	0.063-0.072	0.0042-0.0048	1	14	1
	Spain	SC	HV overall	0.063-0.072	0.0042-0.0048	1	14	1
	Uruguay	EC	broadcast mist blower	0.075-0.090	0.0024-0.003	2	20	1
	USA	SC	spray	0.049-0.098	-	7-14***	30	4
	USA	EC	spray	0.067-0.101	-	7-10***	30	4
Pecans	Mexico	EC	mist blower	0.054-0.108	0.0028-0.0057	2	(f)	1
	USA	SC	applied to run-off	0.073-0.098	-	7-9***	30	4
Persimmon, Japanese	Japan	WP	airblast	0.2	0.004	1-3	21	1
Raspberry	UK	SC	LV overall	0.04	--------	3	14	1
	Ireland	SC	LV overall	0.04	--------	3	14	1
Strawberry	Denmark	EC	HV overall	0.084	--------	3	14	1
	Ireland	SC	LV overall	0.04	--------	NR	14	1
	Italy	EC	HV overall	--------	0.0042-0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0042-0.0048	3	7	1
	Italy	WP	HV overall	0.034-0.038	0.0042-0.0048	3	7	1
	Japan	WP	mist spray[2]	0.03	0.003	1-3	1	1 & 10
	Netherlands[1] (country submission)	EC	spray[2]	0.036-0.084 (depend. on variety)	0.006-0.0084	4	treatment before flowering or after harvest	6
	Netherlands (company submission)	EC	HV overall	0.03-0.05	0.005-0.01	5	treatment before flowering or after harvest	1
	Spain	EC	HV overall		0.0042-0.0048	4	3	1
	Spain	SC	HV overall		0.0036-0.0048	4	3	1

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	UK	SC	LV overall	0.04	-------	NR	14	1

[1] No product label submitted
[2] Glasshouse and Field use
NR No restration restriction, typically 2-4
* max 4 between flowering and benning of ripening
** Application throughout season
*** the maximum number of treatments is controlled by a maximum total dose
Notes (a) to (f) refer to growth stage at last treatment:
(a) immature fruit (b) early fruit
(c) from disease onset (d) mature fruit
(e) fruit initiation (f) pre-flowering

Table 21. Registered uses of fenarimol on vegetables.

Crop	Country	Form	Application				PHI, days	Refer-ence
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Artichokes	Italy	EC	HV overall	--------	0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
Aubergines	Italy	EC	HV overall	--------	0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Japan	WP	mist spray	0.024 ~0.04	0.0012 ~0.002	1-3	1	1
Courgettes	Netherlands[1] (country submission)	EC	spray[2]	0.012-0.036	0.0024	6	3	6
	Netherlands[1] (country submission)	EC	spray (field only)	0.0096-0.024	0.0024	6	3	6
Cucumbers	Brazil	EC	knapsack individ. plant	0.038-0.072	0.0048-0.0072	4	4	1
	Denmark	EC	HV overall[3]	0.024-0.036	0.0024	4-8	2	1
	Ireland	SC	LV overall	--------	0.001-0.002	NR	2	1
	Japan	WP	mist spray	0.024	0.0012	1-3	1	1
	Netherlands	EC	spray[2]	0.012-0.036	0.0024	6	3	1
	UK	SC	LV overall[3]	--------	0.001-0.002	NR	2	1
	Uruguay	EC	knapsack individ. plant	0.014-0.024	0.0012-0.0024	4	4	1
Cucurbits	Australia	EC	Boom	0.024	0.004	1-10	3	1
	Greece	WP	HV overall	0.018-0.024	0.0018-0.0024	as requir ed	1	1
	Italy	EC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	SC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	WP	HV overall	0.020-	0.0024-	3	7	1

Crop	Country	Form	Application				PHI, days	Refer-ence
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
				0.024	0.003			
	Spain	EC	HV overall	0.01-0.019	0.0036-0.0048	2	7	1
	Spain	SC	HV overall	0.013-0.019	0.0042-0.0048	2	7	1
Egg plants, see Aubergines								
Gherkins	Netherlands[1] (country submission)	EC	spray[2]	0.012-0.036	0.0024	6	3	6
	Netherlands[1] (country submission)	EC	spray (field only)	0.0096-0.024	0.0024	6	3	6
Melons	Japan	WP	mist spray	0.024	0.0012	1-4	1	1
	Netherlands	EC	spray[2]	0.012-0.036	0.0024	6	3	1
	Portugal	EC	HV overall	0.024-0.036	0.0024-0.0036	5	3	1
Musk-melons	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
Peas	Italy	EC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	SC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	WP	HV overall	0.02-0.024	0.0024-0.003	3	7	1
Peas, Immature	Japan	WP	mist spray	0.024	0.0012	1-5	1	1
Peppers	Italy	EC	HV overall	--------	0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Netherlands[1] (country submission)	EC	spray[2]	0.012-0.036	0.0024	6	3	6
	Japan	WP	mist spray	0.024	0.0012	1-4	1	1
	Spain	EC	HV overall	0.048-0.072	0.0048-0.006	3	7	1
	Spain	SC	HV overall	0.048-0.072	0.0048-0.006	3	7	1
	UK	SC	overall spray[2]	0.054	0.002	3	7	9
Pumpkins	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
	Japan	WP	mist spray	0.012	0.0012	1-4	3	1
	Peru	EC	gun individ. plant	0.012-0.060	0.0015-0.004	4	4	1
Squash, small	Argentina	EC	gun individ. plant	0.0096-0.024	0.0012-0.0024	4	4	1
Squash	Uruguay	EC	knapsack individ. plant	0.014-0.024	0.0012-0.0024	4	4	1
Squash, summer	Netherlands	EC	spray[2]	0.012-0.036	0.0024	6	3	1
Tomatoes	Denmark	EC	HV overall[3]	0.024-0.036	0.0024	4-8	2	1
	Italy	EC	HV overall	---------	0.0048	3	7	1
	Italy	SC	HV overall	---------	0.0048	3	7	1

Crop	Country	Form	Application				PHI, days	Refer-ence
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Japan	WP	mist spray	0.04	0.002	1-3	1	1
	Netherlands[1] (country submission)	EC	spray[2]	0.024-0.072	0.0048	3	3	6
	Netherlands (company submission)	EC	HV overall	0.024-0.072	0.0048	5	3	1
	Spain	EC	HV overall	0.028-0.057	0.0048	3	7	1
	Spain	SC	HV overall	0.028-0.057	0.0048	3	7	1
	UK	SC	overall spray[2]	0.054	0.002	3	7	9
Watermelons	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
	Japan	WP	mist spray	0.012	0.0012	1-4	3	1
	Uruguay	EC	knapsack individ. plant	0.0096-0.0024	0.0012-0.0024	4	4	1
Vegetables	Netherlands	EC	HV overall	0.012-0.036	0.0024	5	3	1

[1] No product label submitted
[2] Glasshouse use only
[3] Glasshouse and field use

Table 22. Registered uses of fenarimol on hops and cereals.

Crop	Country	Form	Application				PHI, days	Ref.
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.		
Hops	Germany	WP	HV row	0.06	0.0015	max 4	10	1 & 8
	Spain	EC	HV overall		0.0042-0.0048		--------	1
	Spain	SC	HV overall		0.0042-0.0048		--------	1
Wheat	Japan	WP	Boom	0.04-0.06	0.004	1-2	14	1

Uses of fenarimol were also reported in Algeria, Austria, "Belarus", Bulgaria, China, "CR/SR", Croatia, Egypt, Hungary, India, Indonesia, Iraq, Korea, Lebanon, Libya, Macedonia, Morocco, Pakistan, Poland, Romania, Russia, Slovenia, Slovakia, Switzerland, Syria, Taiwan and Tunisia, but insufficient information was submitted for inclusion in the Tables.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The residue trials are summarized in the following Tables. Trials were carried out under field conditions unless stated otherwise. Unless indicated in the notes, trials were reported in sufficient detail and acceptable analytical information was supplied. Analytical recoveries outside the range 70-120% and/or storage of samples for longer than 6 months are also indicated in the notes. Analytical results have been rounded to one significant figure if <0.1 mg/kg except where processing information is given.

Apples. Informatiaon on GAP was reported for many countries world-wide. The maximum

application rates are 0.054-0.14 kg ai/ha with PHIs of 14-35 days.

Residue trials data were available from Belgium, Germany, the UK, Canada, the USA, Chile, Brazil, New Zealand and The Netherlands. Residues in 16 Northern European trials according to German GAP (0.0036 kg ai/hl, 21-day PHI) were 0.02-0.21 mg/kg. Three further trials which reflected German GAP showed residues of 0.06, 0.1 and 0.1 mg/kg but only a summary was submitted. Eight Northern European trials complied with GAP in Denmark, the UK and Ireland in which there is a shorter PHI of 14 days (maximum rates 0.06-0.08 kg ai/ha, concentration not specified) with residue levels of 0.02-0.18 mg/kg. A further 6 Dutch trials were within GAP in The Netherlands (0.0039-0.076kg ai/hl, 21-day PHI) with residues of 0.01-0.34 mg/kg in samples taken 21 days after the final treatment. However, these Dutch trials were submitted in summary form only. In 5 replicated US trials according to GAP (ca 0.1 kg ai/ha, 30-day PHI) residue levels were 0.002-0.3 mg/kg. In three New Zealand trials according to GAP (maximum 0.09 kg ai/ha, 0.003 kg ai/hl, 35-day PHI) residues were 0.008-0.03 mg/kg.

Table 23. European supervised residue trials on apples.

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Ramecroix, Belgium, 1976[1]	EC	11	0.034	0.004	0	0.12	NF 13 B76-001
					7	0.07	
					14	0.05	
					21	0.06	
					28	0.04	
					85	0.01	
Giessen, Germany, 1977[1]	EC	10	0.036	0.003	55	<0.01	NF 15 D76-302
			0.048	0.004	55	<0.01	
Giessen, Germany, 1978[2,3,5]	EC	14	0.054	0.0036	0	0.13	NF 08 D78-311
					3	0.12	
					7	0.10	
					10	0.11	
					14	0.07	
					21	0.06	
					28	0.08	
					36	0.07	
Giessen, Germany, 1981[3,5]	SC	14	0.054	0.0036	0	0.16	NF 20 D81-302
					4	0.06	
					13	0.05	
					20	0.07	
					27	0.04	
					33	0.06	
Uberlingen, Germany, 1981[3,4,5]	SC	14	0.054	0.0036	0	0.29	NF 20 D81-353
					4	0.34	
					7	0.02	
					14	0.02	
					21	0.02	
Wulfsdorf, Germany, 1981[3,5]	SC	13	0.054	0.0036	0	0.36	NF 20 D81-350
					7	0.23	
					14	0.18	
					22	0.06	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					28	0.05	
					35	0.05	
Wittlich, Germany, 1981[3,4,5]	SC	10	0.06	0.00396	0	0.37	NF 20 D81-351
					7	0.19	
					14	0.15	
					21	0.15	
					28	0.09	
					63	0.01	
Kriftel, Germany, 1982[3,5]	EC	13	0.036	0.0036	0	0.06	NF 21 D82-304
					8	0.05	
					14	0.04	
					17	0.04	
	SC	13	0.036	0.0036	0	0.1	
					8	0.09	
					14	0.07	
					17	0.04	
Kriftel, Germany, 1982[3,5,6]	EC	13	0.036	0.0036	0	0.09	NF 21 D82-305
					8	0.08	
					14	0.06	
					21	0.05	
					30	0.03	
	SC	13	0.036	0.0036	0	0.21	
					8	0.17	
					14	0.04	
					21	0.11	
					30	0.05	
Marbach, Germany, 1982[3,5]	EC	14	0.036	0.0036	0	0.37	NF 21
					7	0.24	
					13	0.22	
					20	0.21	
					27	0.14	
Marbach, Germany, 1982[3,5]	EC	14	0.036	0.0036	0	0.18	NF 21 D82-307
					7	0.11	
					13	0.15	
					20	0.14	
					27	0.09	
Giessen, Germany, 1982[3,5,6]	EC	14	0.036	0.0036	0	0.17	NF 21 D82-301
					5	0.08	
					13	0.05	
					19	0.03	
					26	0.04	
					35	0.01	
	SC	14	0.036	0.0036	0	0.19	
					5	0.11	
					13	0.08	
					19	0.07	
					26	0.04	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					35	0.02	
Giessen, Germany, 1982[3,5]	SC	14	0.036	0.0036	0	0.10	NF 21 D82-302
					5	0.12	
					13	0.06	
					19	0.04	
					26	0.04	
					35	0.03	
	EC	14	0.036	0.0036	0	0.10	
					5	0.07	
					13	0.03	
					19	0.03	
					26	0.01	
					35	0.02	
Giessen, Germany, 1982[3,5,6]	EC	14	0.036	0.0036	0	0.06	NF 21 D82-303
					8	0.03	
					14	0.03	
					21	0.02	
					30	0.01	
	SC	14	0.036	0.0036	0	0.10	
					8	0.09	
					14	0.01	
					21	0.03	
					30	0.01	
Bonn, Germany, 1982[1]	EC	12	0.05	0.004	0	0.1	8
					7	0.1	
					14	0.1	
					21	0.1	
					28	0.04	
Dossenheim, Germany, 1982[1]	EC	14	0.05	0.004	0	0.1	8
					10	0.1	
					14	0.04	
Frankfurt, Germany, 1982[1]	EC	14	0.05	0.004	0	0.1	8
					10	0.1	
					14	0.1	
					21	0.1	
					28	0.02	
Oudenbosch, Netherlands, 1977[5,7]	WP	1		0.005	7	0.14	6
						0.14	
						0.22	
						0.17	
					14	0.1	
						0.14	
						0.15	
						0.09	
					21	0.09*	
						0.01*	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
						0.11*	
						0.06*	
Berlicum, Netherlands, 1977[5,7]	WP	1		0.005	7	0.33	6
						0.41	
						0.3	
						0.37	
					14	0.21	
						0.46	
						0.35	
						0.24	
					21	0.28*	
						0.21*	
						0.26*	
						0.34*	
Breskens, Netherlands, 1977[5,7]	WP	1		0.005	7	0.27	6
						0.34	
						0.22	
						0.19	
					14	0.16	
						0.12	
						0.13	
						0.15	
					21	0.22*	
						0.22*	
						0.18*	
						0.14*	
Knuiningen, Netherlands, 1978[5,7]	WP	1		0.005	8	0.09	6
					15	0.11	
					22	0.06*	
Knuiningen, Netherlands, 1978[5,7]	WP	1		0.005	9	0.09	6
					15	0.06	
					22	0.03*	
Knuiningen, Netherlands, 1978[5,7]	WP	1		0.005	7	0.14	6
					14	0.11	
					21	0.13*	
Surrey, UK, 1981[3,5]	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.17	NF 20 FF81-002-01
					7	0.12	
					14	0.04	
					21	0.07	
Surrey, UK, 1981[3,5]	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.30	NF 20 FF81-002-02
					7	0.18	
					14	0.10	
					21	0.09	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Surrey, UK, 1981[3,5]	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.31	NF 20 FF81-002-03
					7	0.19	
					14	<u>0.14</u>	
					21	0.13	

Underlined residues are from treatments according to GAP in Germany; those underlined twice from treatments according to GAP in Denmark, Ireland and the UK.
* According to GAP in The Netherlands.
[1] No detailed report submitted
[2] No weather data submitted
[3] Method of analysis unspecified
[4] Crops stored for 7 (NF20 D81-351) or 8 months (NF20 D81-353) before analysis
[5] No example chromatograms submitted
[6] High associated recoveries (NF21: D82-305 113-126%; D82-301 102-126%; D82-303 110-127%)
[7] Report not in English

Table 24. Non-European supervised residue trials on apples (including US processing trials).

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Ontario, Canada, 1975[1,2,7]	EC	13	0.025	0.002	42	fruit	0.01	NF 25 MFM 5-1
			0.05	0.004		fruit	0.02	
			0.075	0.008		fruit	0.04	
Ontario, Canada, 1975[1,2,7]	EC	13	0.025	0.002	42	fruit	0.02	NF 25 MFM 6-1
			0.03	0.004		fruit	0.02	
			0.05	0.004		fruit	0.02	
			0.075	0.008		fruit	0.06	
Ontario, Canada, 1976[1,2,7]	EC	12	0.097	0.002	34	fruit	0.01	NF 25 MFM 6-3
			0.134	0.004		fruit	0.02	
			0.270	0.004		fruit	0.06	
		11	0.16 x 4 0.08 x 7	0.004 x 4 0.002 x 7		fruit	0.04	
Meaford, ONT, Canada, 1977 [1,2,7,9]	EC	6	0.016			fruit	0.007	NF 26 MFM 7-12
		6			15	fruit	0.05	
Bowmanville, ONT, Canada, 1977[1,2,7,9]	EC	5	0.016			fruit	0.17	NF 26 MFM 7-14
London, ONT, Canada, 1977[1,2,7,9]	EC	8	0.012		28	fruit	0.02	NF 26 MFM 7-28
Simcoe, ONT, Canada, 1977[1,2,7,9]	EC	8	0.012		84	fruit	0.03	NF 26 MFM 7-29
Simcoe, ONT, Canada, 1977[1,2,7,9]	EC	10	0.016 x 8 0.08 x 2			fruit	0.03	NF 26 MFM 7-31
		10	8 x 0.141 or 0.016 2 x 0.069 or			fruit	0.03	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
			0.08					
Nattawa, ONT, Canada, 1977[1,2,7,9]	EC	6	0.016		83	fruit	0.007	NF 26 MFM 7-34
		6	0.016		83	fruit	0.003	
Meaford, ONT, Canada, 1977[1,7]	EC	6	0.142		15	fruit	0.07	NF 27 MFM 7-12
		6	0.142			fruit	0.05	
Bowmanville, ONT, Canada, 1977[1,7]	EC	5	0.142		69	fruit	0.02	NF 27 MFM 7-14
London, ONT, Canada, 1977[1,7]	EC	8	0.1		28	fruit	0.02	NF 27 MFM 7-38
Simcoe, ONT, Canada, 1977[1,7]	EC	8	0.1		86	fruit	0.03	NF 27 MFM 7-29
Simcoe, ONT, Canada, 1977[1,7]	EC	8	6 x 0.142 2 x 0.071		45	fruit	0.03	NF 27 MFM 7-33
Simcoe, ONT, Canada, 1977[1,7]	EC	6	0.142		90	fruit	0.003	NF 27 MFM 7-34
Nottawa, ONT, Canada, 1977[1,7]	EC	6	0.142		90	fruit	0.007	NF 27 MFM 7-34
Oyamba, BC, Canada, 1980[1,7]	EC	3	0.101		131	fruit	0.003	NF 27 K Ellison
					95	fruit	0.004	
Kelowna, BC, Canada, 1980[1,7]	EC	3	0.101		121	fruit	<0.002	NF 27 E. Star
West Bank, BC, Canada, 1980[1,7]	EC	3	0.101		121	fruit	0.03 <0.002	NF 27 M. Janse
Campinas, Brazil, 1985[1,6,7]	EC	9		0.018	28	fruit	0.01	NB 29
				0.036		fruit	0.04	
Curico, Chile, 1980[1,3,7,12]	EC	9	0.06		100	fruit	0.09 0.09	NF 28
	SC					fruit	0.06	
San Fernando, Chile, 1980[1,3,7,12]	EC	6	0.06		113	fruit	0.08	
			0.048			fruit	0.003	
Albany, NZ, 1976[1]	EC	10	0.132	0.002-0.004	2	fruit	0.07	NF 29 NZ 75-19
					6	fruit	0.05	
					12	fruit	0.04	
			0.099	0.0015-0.003	2	fruit	0.07	
					6	fruit	0.05	
					7	fruit	0.07	
					21	fruit	0.06	
					35	fruit	0.02	
Hastings, NZ, 1979[1]	WP	12	0.061	0.0025	52	fruit	0.008	NF 29 NZ 78-2
			0.061	0.003		fruit	0.006	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Hamilton, NZ, 1980[1]	WP	1	0.048		120	fruit	<0.002	NF 29 NZ 80-6
Hamilton, NZ, 1980[1]	WP	8	0.081		1	fruit	0.02	NF 29 NZ 80-5
					8	fruit	0.02	
					15	fruit	0.01	
					29	fruit	0.008	
Christchurch, NZ, 1981[1]	WP	14		0.003	31	fruit	0.03	NF 29 T Holland
					38	fruit	0.03	
					45	fruit	0.01	
Geneva, NY, USA, 1981[1,2,4]	EC	6	0.0445		107	fruit	<0.002	NF 18 Cornel
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.003	
						dry pomace	0.025	
		3 3	0.0445 0.0223		107	fruit	0.002	
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.002	
						dry pomace	0.014	
Biglerville, PA, USA, 1981[1,2,4,9]	EC	11	0.1038		42	fruit	0.037	NF 18 Penn. Univ.
						juice	0.003	
						sauce	0.009	
						wet pomace from sauce	0.20	
						dry pomace	0.67	
		4 7	0.1038 0.0519		42	fruit	0.017	
						juice	<0.002	
						sauce	0.004	
						wet pomace from sauce	0.079	
						dry pomace	0.20	
Winchester, VA, USA, 1981[1,2,4,9]	EC	10	0.1038		34	fruit	0.059	NF 18 Winchester
						juice	0.002	
						sauce	0.015	
						wet pomace from sauce	0.14	
						dry pomace	0.31	
		3 7	0.1038 0.0519			fruit	0.057	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						juice	0.002	
						sauce	0.01	
						wet pomace from sauce	0.015	
						dry pomace	0.36	
Sodus, NY, USA, 1982[1,2,3,4,9,12]	EC	1 10	0.316 0.105		41	juice	0.002	NF 18 CMR 82-9
						wet pomace from juice	0.049	
						sauce	<0.002	
						dry pomace	0.11	
		1 10	0.316 0.105		41	juice	<0.002	
						wet pomace from juice	0.061	
						sauce	<0.002	
						dry pomace	0.13	
Sodus, NY, USA,1982[1,2]	EC	8	0.105		63	fruit	0.014	NF 18 CMR 8-10
						juice	0.002	
						wet pomace from juice	0.073	
						sauce	<0.002	
						dry pomace	0.12	
		8	0.105		63	fruit	0.008	
						juice	0.002	
						wet pomace from juice	0.072	
						sauce	<0.002	
						dry pomace	0.16	
Sodus, NY, USA, 1982[1,2]	EC	8	0.079		83	fruit	<0.002	NF 18 CMR 82-11
						juice	<0.002	
						wet pomace from juice	0.006	
						sauce	<0.002	
						dry pomace	0.012	
		8	0.079		83	fruit	<0.002	
						juice	0.002	
						wet pomace from juice	0.003	
						sauce	<0.002	
						dry pomace	0.013	
Sodus, NY, USA, 1982[1,2]	EC	10	0.0789		53	fruit	0.007	NF 18 CMR 82-16
						juice	<0.002	
						sauce	<0.002	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						wet pomace from sauce	0.068	
						dry pomace	0.12	
		10	0.0789		53	fruit	0.007	
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.079	
						dry pomace	0.098	
Daleville, VA, USA, 1982[1,2,4]	EC	8	0.1052		33	fruit	0.002	NF 18 DAA 82-6
						juice	<0.002	
						wet pomace from juice	0.013	
		11	0.1052		33	fruit	0.002	
						juice	<0.002	
						wet pomace from juice	0.009	
Tehachapi, CA, USA, 1982[1,2,9]	EC	4	0.2105		118	fruit	<0.002	NF 18 DHF 82-12
						juice	<0.002	
						wet pomace from juice	0.009	
Gardners, PA, USA, 1982[1,2,11]	EC	8	0.0526		136	fruit	<0.002	NF 18 PEB 82-5
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	<0.002	
Thurmont, MD, USA, 1982[1,2]		10	0.1052		70	fruit	0.02	NF 18 PEB 82-6
						juice	0.002	
						sauce	0.003	
						wet pomace from sauce	0.036	
Gettysburgh, PA, USA, 1982[1,2,11]		10	0.0526		75	fruit	0.021	NF 18 PEB 82-14
						juice	0.003	
						sauce	<0.002	
						wet pomace from sauce	0.054	
Watsonville, CA, USA,1982[1,2,9]		4	0.1052		104	fruit	0.005	NF 18 RAH 82-1
						juice	0.002	
						wet pomace from juice	0.018	
		4	0.2105		104	fruit	0.013	
						juice	0.003	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						wet pomace from juice	0.043	
Snelling, CA, USA, 1982[1,2,9]		4	0.1052		93	fruit	0.008	NF 18 RAH 82-2
						juice	0.002	
						wet pomace from juice	0.021	
		4	0.2105		93	fruit	0.011	
						juice	0.002	
						wet pomace from juice	0.029	
Moxee, WA, USA, 1982[1,2]		1 3	0.084 0.104		122	fruit	0.002	NF 18 WTC 82-4
						juice	<0.002	
						wet pomace from juice	0.005	
		1 3	0.104 0.132		122	fruit	0.002	
						juice	<0.002	
						wet pomace from juice	0.004	
Orondo, WA, USA, 1982[1,2]		2 2	0.105 0.132		147	fruit	0.007	NF 18 WTC 82-8
						juice	<0.002	
						wet pomace from juice	0.015	
Covert, MI, USA, 1982[1,2,9]		10	0.1052		147	fruit	0.019	NF 18 DG 082-10
						juice	<0.002	
						wet pomace from juice	0.14	
						sauce	0.003	
						wet pomace from sauce	0.33	
Sodus, NY, USA, 1976[1,2]		10	0.1075		62	fruit	0.004	NF 18 CDC 6-16
						juice	<0.002	
						wet pomace from juice	0.022	
						dry pomace	0.068	
Reedley, CA, USA, 1988	EC	7	0.105		30	fruit	0.03	NF 31 DHF88-02
		7	0.105		30	fruit	0.02	NF 31 DHF 88-03
Sunnyside, WA, USA, 1988	EC	7	0.105		29	fruit	0.01	NF 31 BJB88-01
		7	0.105		29	fruit	0.01	NF 31 BJB88-02
		7	0.105		29	fruit	0.02	NF 31

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
								BJB88-03

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in New Zealand
[1] No weather data submitted
[2] Method of analysis unspecified. Stated to be GLC for studies NF 20, 25 & 26 but no further details
[3] No control plot data submitted
[4] Crops stored for 8-15 months before analysis
[6] No example chromatograms submitted
[7] Duration of sample storage unspecified
[9] High associated recoveries (NF26: MFM 7-12 98-140%, NF 18 dry pomace 132%; juice 121-128%
[11] Half sprayed - one side of row only
[12] System recoveries only submitted (i.e control extract or extraction solvent, not the commodity, was fortified)

Pears. GAP was reported for many countries world-wide and was generally the same as that reported for apples.

A few trials were available which complied with GAP (the same as for apples) in Germany (one trial), Italy (one trial) or the USA (4 trials with replicates), but the recoveries associated with the German (0.13 mg/kg) and Italian trials (0.09 mg/kg) were low at 67 and 63% respectively. Residues in the US trials were 0.01-0.04 mg/kg.

Table 25. Supervised residue trials on pears.

Location, year	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
Australia, 1985[1,5,6]				0.0036	14	0.03	NB 30 AUS 78-314
				0.0072		0.04	
Giessen, Germany, 1978[1-4,6]	EC	14	0.054		0	0.1	NF 03 D78-312
					3	0.08	
					10	0.07	
					13	0.08	
					17	0.08	
					20	0.09*	
					24	0.03	
					31	0.06	
Baricella, Italy, 1981[1-4]	SC	17		0.004	20	0.13	NF 06 181 211
Hood River, OR, USA, 1983[1,5]	EC	3	0.143		112	0.003	NF 33 WTC83-2
Medford, OR, USA, 1983[1,5]	EC	2	0.143		120	<0.001	NF 33 830R12
					144	<0.001	
Hood River, OR, USA, 1984[1,5]	EC	3	0.092		120	<0.001	NF 33 840R4
			0.143		123	<0.001	
Medford, OR, USA, 1985[1,5]	EC	2	0.092 0.071		147	<0.001	NF 33 840R5
			0.143 0.109			<0.001	
Clayton, NC, USA, 1986[1,5]	SC	7	0.1		30	0.01	NF 33 DAA86-13
		7	0.1			0.02	
Reedley, CA, USA, 1986	SC	7	0.1		30	0.03	NF 33 DHF86-5

Location, year	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
	EC					0.01	
Parlier, CA, USA, 1986[1,5]	EC	7	0.1		29	0.04	NF 33 DHF86-6
Mesa, WA, USA, 1986[1,5]	EC	7	0.1		28	0.02	NF 33 DHF86-8
	SC					0.08	

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in Italy
* according to GAP in Germany
[1] No weather data submitted
[2] Method of analysis unspecified
[3] Low associated recoveries (NF03 D78-312 67%; NF06 181-211 63%
[4] No example chromatograms submitted
[5] Duration of sample storage unspecified
[6] Crop variety unspecified

Peaches. GAP was reported for Uruguay, Argentina, Japan, Greece, Italy and Spain. No GAP was reported for apricots or nectarines, although some trials data were submitted. The maximum application rates are 0.036-0.2 kg ai/ha (0.0024-0.0048 kg ai/hl) with a PHI of 1-20 days.

Residue trials were available only from Spain, Italy and France. The critical European GAP for peaches was the Spanish (0.0048 kg ai/hl, PHI 7 days) for which there were 5 trials (one of them replicated) with residues of 0.03-0.3 mg/kg. In two of these trials the volume of spray per hectare was not specified. A further Spanish trial on apricots in 1988 where the use pattern was the same as the Spanish GAP for peaches with a residue of 0.36 mg/kg at 7 days provided supporting information. A single Chilean trial on nectarines reflected the Argentinian GAP for peaches (0.072 kg ai/ha, PHI 20 days) with no residue detected. No data on supervised trials were available for Japanese GAP in which there is a 1-day PHI.

Table 26. Supervised residue trials on peaches, apricots and nectarines.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Fronton, S. France, 1993[1]	EC	3	0.04	0.0078	0	pulp	0.13	NG 07 R93-46
					6		0.04	
					10		0.06	
					13		0.04	
Fronton, France, 1994	EC	5	0.04	0.008	8	pulp	0.03	NG 11 GHE-P-4062
Follonica, Italy, 1977[2-6]	WP	8		0.0042	34	fruit	<0.01	NG 01 I77-212A
Puntone, Italy, 1977[2-6]	WP	4		0.0042	20	fruit	0.02	NG 02 I77-213
Follonica, Italy, 1977[2-6]	WP	6	0.24	0.0042	16	fruit	<0.01	NG 03 I77-214
S. Biagio, Italy, 1993[1]	SC	5	0.09	0.0042	0	pulp	0.44	NG 08 R93-45
					7		0.13	
					10		0.08	
					14		0.08	
			0.1	0.0048	0	pulp	0.65	
					7		0.15	
					10		0.15	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					14		0.16	
Francolino, Italy, 1994	SC	4	0.066 0.069 0.071 0.072	0.0048 x 4	13	pulp	0.05	NG 10 GHE-P-4014
Luchente, Spain, 1988[2,3,5,6,7]	EC	1	0.18	0.0048	0	fruit	0.41	ref. 13
					3		0.38	
					7		0.30	
					14		0.12	
					21		0.10	
Pobla del Duc, Spain, 1992[2,3,5,6,7]	EC	1		0.0036	0	fruit	0.18	ref. 13
					7		0.08	
					14		0.03	
					21		0.02	
Pobla del Duc, Spain, 1993[2,3,5,6,7]	EC	1		0.0036	0	fruit	0.07	ref. 13
					7		0.03	
					14		0.02	
					21		0.01	
NECTARINE								
Chile[2,5,7]	EC		0.072	0.0036	0	fruit	0.03	NG 09
					6		<0.01	
					16		ND	
					24		ND	
APRICOT								
Luchente, Spain, 1988[2,3,5,6,7]	EC	1	0.18	0.0048	0	fruit	0.45	ref. 13
					3		0.44	
					7		0.36	
					14		0.14	
					21		0.08	

Underlined residues are from treatments according to GAP in Spain
Results underlined twice reflect GAP in Argentina
ND - not detected
[1] Crops stored for 11 months before analysis
[2] No weather data submitted
[3] Method of analysis unspecified (reports 2, 3, 4 & 5 in Spanish
[4] Low associated recoveries (NG01 69%; NG02 68%; NG03 59%
[5] No example chromatograms submitted
[6] Duration of sample storage unspecified
[7] No English translation provided

Cherries. GAP was reported for Denmark, Japan and the USA. The maximum application rates reported were 0.06 to about 0.2 kg ai/ha with PHIs of 0-14 days.

All 15 trials submitted were from the USA with samples being taken at 0 and 1 day after the final treatment. In all these trials no account was taken of the weights of the stones. US GAP (0.101 kg ai/ha) allows treatment 'up to and after harvest' and residues in the 9 trials (3 of which were replicated) complying with it were 0.06-0.89 mg/kg.

Table 27. Supervised residue trials on cherries in the USA.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Traverse City, MI, 1987[1,2]	EC	6	0.053		0	fruit pulp	0.21	NG 04 87MI1
					1		0.24	
Geneva, NY, 1987[1,2]	EC	5	0.095		0	pulp	0.07	NG 04 87NY1
					1		0.10	
Biglerville, PA, 1987[1,2]	EC	5	0.089		0	pulp	0.10	NG 04 87PA1
					1		0.11	
Hart, MI, 1987[1,2]	EC	5	0.053		0	fruit	0.16	NG 04 WWH87-2
					1		0.17	
Hart, MI, 1987[1,2]	EC	5	0.053		0	pulp	0.18	NG 04 WWH87-3
					1		0.13	
Sutton Bay, MI, 1987[1,2]	EC	5	0.053		0	pulp	0.28	NG 04 WWH87-5
					1		0.26	
Sutton Bay, MI, 1987[1,2]	EC	6	0.053		0	pulp	0.20	NG 04 WWH87-6
					1		0.10	
Sutton Bay, MI, 1987[1,2]	EC	5	0.053		0	pulp	0.17	NG 04 WWH87-7
					1		0.16	
Vantage Bay, WA, 1987[1,2]	EC	4	0.105		0	pulp	0.06	NG 04 WTC87-3
					1		0.05	
Malago, WA, 1987[1,2]	EC	4	0.105		0	pulp	0.44	NG 04 WTC87-6
					1		0.41	
Othello, WA, 1987[1,2]	EC	4	0.105		0	pulp	0.17	NG 04 WTC87-7
					1		0.15	
Corvallis, MI, 1987[1,2]	EC	4	0.105		0	pulp	0.63	NG 04 WTC87-8
					1		0.64	
Linden, CA, 1989	EC	4	0.106		0	fruit	0.89	NG 05 LES89-05
					1		0.49	
			0.106	0.0056	0	fruit	0.77	
					1		0.63	
Grevais. OR, 1989	EC	4	0.106	0.0056	0	fruit	0.22	NG 05 LR89-01
					1		0.28	
	SC	4	0.106	0.0056	0	fruit	0.1	
					1		0.1	
Westley, CA,1989	EC	4	0.106	0.0056	0	fruit	0.4	NG 05 LES89-04
					1		0.88	
	SC	4	0.106	0.0056	0	fruit	0.3	
					1		0.25	

Underlined residues are from treatments according to GAP in the USA
[1] No weather data submitted
[2] Duration of sample storage unspecified

Currants. GAP for blackcurrants was reported for Denmark, Ireland and the UK, and for all currants for The Netherlands. The application rates were 0.04-0.06 kg ai/ha or 0.0048 kg ai/hl with PHIs of 14 or 21 days.

Data were available only from 5 trials in The Netherlands. Residues were 0.04-0.74 mg/kg 15 days after the final treatment but with a variety of application rates with only one trial according to the reported GAP.

Gooseberries. GAP in Ireland and The Netherlands is the same as for currants. Only one trial in The Nethlands was reported with a residue of 0.05 mg/kg at 10 days and this trial was submitted in summary form only.

Table 28. Supervised residue trials on currants and gooseberries in The Netherlands in 1980. All EC applications. All reference 6.

Crop	Application			PHI, days	Residues, mg/kg
	No.	kg ai/ha	kg ai/hl		
Blackcurrant[1,2]					
	8		40ppm	2	0.1
				10	0.07
				14	0.04
				22	0.05
				29	0.06
	1	6-	60 ppm	13	0.47
	1		80 ppm	13	0.45
	?	0.06		50	0.10
	?	0.08		13	0.74
Redcurrant[1,2]					
	3	0.048		25	0.07
					0.14
					0.06
					0.08
Gooseberry[1,2]					
	8		40ppm	2	0.07
				10	0.05

Underlined residues are from treatments according to GAP in The Netherlands
[1] No example chromatograms submitted
[2] No English translation provided

Grapes. GAP was reported for many countries world-wide. The maximum application rates were 0.012-0.06 kg ai/ha with PHIs of 7-35 days. CLICK HERE to continue

Residue trials were available from Germany, France, Austria, Italy, the USA, Brazil and Australia. A number of German trials were submitted of which six (2 with replicates) were according to German GAP (0.0234 kg ai/ha, 35-day PHI). The residues in these were 0.01-0.15 mg/kg in samples taken 35 days after the final treatment. Seven of the German trials (two with replicates) were at or within the UK GAP (0.04 kg ai/ha, PHI of 14 days) with residues of 0.02-0.24 mg/kg in samples taken 14 days after the final treatment. In a single French trial conducted in accordance with GAP in France (0.018 kg ai/ha, PHI 7 days) a residue of 0.02 mg/kg was found after 9 days.

Residues in trials according to US GAP (0.051 kg ai/ha, 30-day PHI) were low (0.003-0.06 mg/kg) in 17 US trials, several of which were replicated, in samples taken 28-32 days after the final treatment. Australian GAP (0.024 kg ai/ha or 0.0024 kg ai/hl, 14-day PHI) was also supported by 5 trials with either the maximum spray concentration or application rate per hectare (both are stated on the product label). Residues were 0.01-0.08 mg/kg 13 or 14 days after the final treatment.

None of the Southern European trials according to GAP conformed to Italian (0.06kg ai/ha or 0.0036 kg ai/hl, 14-day PHI) or Portuguese GAP (0.03kg ai/ha or 0.003 kg ai/hl, 7-day PHI) which have the highest dose rate and the shortest PHI respectively.

Table 29. European supervised residue trials on grapes.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Rohrendorf, Austria, 1977[1,2,5,6]	EC	4	0.036	0.0036	58	fruit	<0.01	NH 05
Rohrendorf, Austria, 1977[1,2,5,6]	WP	4	0.036	0.0036	58	fruit	0.01	NH 05
Grosshofflein, Austria, 1977[1,2,5,6]	EC	4	0.024	not reported	66	fruit	0.02	NH 06
		4	0.036	0.0036	66	fruit	<0.01	
Pau, France, 1981[5]	SC	4	0.024	0.024 Low vol.	0	fruit	0.18	NH 12
					7	fruit	0.12	
					14	fruit	0.05	
		4	0.036	0.036 Low vol.	0	fruit	0.27	
					7	fruit	0.18	
					14	fruit	0.04	
Sistels, France, 1993[3]	SC	3	0.018	0.075 Low vol.	0	fruit	0.04	NH 04
					4	fruit	0.03	
					9	fruit	0.02	
					15	fruit	0.02	
Godramstein, Germany, 1992[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.02	NH 11
					35	fruit	0.03	
					42	fruit	0.01	
					35	must	<0.01	
					35	wine	<0.01	
Londau, Germany, 1992[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.04	NH 11

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
					35	fruit	0.04	
					42	fruit	0.02	
					35	must	<0.01	
					35	wine	<0.01	
Neustadt, Germany, 1993[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.02	NH 11
					35	fruit	0.01	
					42	fruit	0.02	
					35	must	<0.01	
					35	wine	<0.01	
Neustadt, Germany, 1993[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.02	NH 11
					35	fruit	0.02	
					42	fruit	0.01	
					35	must	<0.01	
					35	wine	<0.01	
Bad Kreuznach, Germany, 1982 [5]	SC	8	0.005-0.033	2X0.0016 6X0.0031	0	fruit	0.23	NH 12
					7	fruit	0.14	
					14	fruit	0.14*	
					21	fruit	0.10	
					28	fruit	0.11	
					35	fruit	0.07	
					42	fruit	0.08	
Ortsweil Wolf, Germany, 1982 [5]	EC	6	0.014-0.04	2X0.0008 4X0.0016	0	fruit	0.56	NH 12
					7	fruit	0.22	
					14	fruit	0.20*	
					21	fruit	0.10	
					28	fruit	0.07	
					35	fruit	0.06	
					42	fruit	0.05	
Ortsweil Wolf, Germany, 1982 [5]	SC	6	0.014-0.04	2X0.0008 4X0.0016	0	fruit	0.44	NH 12
					7	fruit	0.28	
					14	fruit	0.18*	
					21	fruit	0.10	
					28	fruit	0.07	
					35	fruit	0.05	
					42	fruit	0.05	
Trier, Germany, 1982 [5]	SC	6	2X0.012 4X0.024	2X0.0008 4X0.0016	0	fruit	0.02	NH 12

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
					7	fruit	0.03	
					14	fruit	0.02*	
					21	fruit	0.01	
					28	fruit	0.01	
					35	fruit	0.01	
					42	fruit	0.01	
		8	1X0.014 7X0.028	1X0.0008 7X0.0016	0	fruit	0.33	
					7	fruit	0.24	
					14	fruit	0.24*	
					21	fruit	0.23	
					28	fruit	0.19	
					35	fruit	0.15	
					42	fruit	0.14	
Trier, Germany, 1982 [5]	EC	6	2X0.012 4X0.024	2X0.0008 4X0.0016	0	fruit	0.03	NH 12
					7	fruit	0.02	
					14	fruit	0.02*	
					21	fruit	0.01	
					28	fruit	0.01	
					35	fruit	0.01	
					42	fruit	0.01	
		8	1X0.014 7X0.028	1X0.0008 7X0.0016	0	fruit	0.17	
					7	fruit	0.16	
					14	fruit	0.10*	
					21	fruit	0.09	
					28	fruit	0.09	
					35	fruit	0.10	
					42	fruit	0.11	
Thringen, Germany, 1982[5]		8	2X0.015 6X0.039	1X0.0008 7X0.0020	0	fruit	0.20	NH 12
					7	fruit	0.14	
					14	fruit	0.18*	
					21	fruit	0.11	
					28	fruit	0.08	
					35	fruit	0.08	
					42	fruit	0.08	
Bad Kreuznach, Germany, 1982[5]	EC	8	2X0.015 6X0.039	1X0.0008 7X0.0020	0	fruit	0.08	NH 12
					7	fruit	0.06	
					14	fruit	0.07*	
					21	fruit	0.05	
					28	fruit	0.03	
					42	fruit	0.05	
					35	fruit	0.03	
Calderara, Italy, 1977[1,2,4-6]	WP	7	0.024	not reported	22	fruit	0.02	NH 09

Underlined residues are from treatments according to GAP in Germany; the residue underlined twice was from treatment according to GAP in France
* according to UK GAP.
[1] No weather data submitted
[2] Method of analysis unspecified
[3] Crops stored for more than 6 months before analysis (8-9 months except wine samples)
[4] Low associated recoveries (63%)
[5] No example chromatograms submitted
[6] Duration of sample storage unspecified

Table 30. Non-European supervised residue trials on grapes (including US processing trials).

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Sungarden, Australia, 1976[1,2]	EC	2	0.015	0.003	71	fruit	--	NH 22 AUS 76-237
		2	0.01	0.002	71	fruit	0.001	
		2	0.02	0.004	71	fruit	0.005	
Victoria, Australia, 1976[1,2,4]	EC	2	0.01	0.002	89	fruit	0.001	NH 22 AUS 76-238
		2	0.015	0.003	89	fruit	0.001	
		3	0.03	0.02	66	fruit	0.001	
		3	0.045	0.003	66	fruit	0.001	
		3	0.06	0.004	66	fruit	0.002	
Mclaren Vale, S. Australia, 1978[1,2]	EC	4	0.09	0.0036	90	fruit	0.009	NH 22 AUS 78-263
Pokolbin, NSW, Australia, 1980[1,2]	EC	7	0.01	0.001	8	fruit	0.05	NH 22 AUS 79-339
		7	0.024		8	fruit	0.06	
Mclaren Vale, S. Australia, 1981 (1,7)	EC	4		0.0024	0	fruit	0.34	NH 23 AUS 80-223
					1	fruit	0.19	
					5	fruit	0.09	
					29	fruit	0.02	
		4		0.0036	0	fruit	0.72	
					1	fruit	0.43	
					5	fruit	0.27	
					29	fruit	0.10	
Lyndoch, S. Australia, 1981[1,2]	EC	4	0.047	0.0024	0	fruit	0.28	NH 22 AUS 83-201
					7	fruit	0.22	
					14	fruit	<u>0.06</u>	
					28	fruit	0.02	
		4	0.094	0.0048	0	fruit	0.45	
					7	fruit	0.37	
					14	fruit	0.19	
					28	fruit	0.10	
Pokolbin, NSW, Australia, 1985[1,3]	EC	4		0.0024	7	fruit	0.02	NH 23 F/H01/85
					13	fruit	<u>0.01</u>	
					20	fruit	0.001	
					27	fruit	0.01	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
		4		0.0048	7	fruit	0.06	
Irymple, Australia, 1992[1,2,4]	EC	1	0.037	0.0024	0	fruit	1.01	NH 24 S93 FEN1
					1		0.84	
					3		0.46	
					7		0.11	
					14		0.06	
					22		0.03	
					35		<0.2	
Irymple, Australia, 1993[1,2,4]	EC	1	0.037	0.0024	0	fruit	0.23	NH 24 S93 FEN3
					1		0.2	
					3		0.16	
					7		0.08	
					14		0.05	
					21		0.03	
					14	wine	0.008	
					14	dried fruit	0.03	
Nuriootpa, Australia, 1993[1,2,4]	EC	1	0.024	0.040-0.074	0		0.06	NH 24 A93 FEN2
					1		0.06	
					3		0.18	
					5		0.05	
					7		0.05	
					14		0.08	
					21		0.05	
					28		0.04	
					28	wine	0.008	
Nuriootpa, Australia, 1993[1,2,4]	EC	6	0.048	0.080- 0.148	28	fruit	0.57	NH 24 A93 FEN4
Brazil, 1985[1,2,4,7]	EC	11	0.024	0.0024	28	fruit	0.03	NB 29
Fresno, CA, USA, 1981[1,2]	EC	4	0.019 0.028 0.037 0.037		62	fruit	0.008	NH 21 DHF81-3
Fresno, CA, USA, 1981[1,2]	EC	3	0.025 0.025 0.025		70	fruit	<0.002	NH 21 DHF81-4
		4	0.037 0.056 0.074		70	fruit	0.006	
		3	0.025 0.025 0.025		70	fruit	0.002	
		3	0.012 0.025 0.037		70	fruit	0.003	
Fresno, CA, USA, 1981[1,2]	SC	3	0.019 0.028 0.037		70	fruit	0.005	NH 21 DHF81-4
		3	0.037		70	fruit	0.005	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
			0.037 0.037					
		3	0.037 0.037 0.037		70	fruit	0.002	
			0.012 0.025 0.037		70	fruit		
Fresno, CA, USA, 1981[1,2]	SC	3	0.074 0.111 0.148		70	fruit	0.02	NH 21 DHF81-5
	EC	3	0.037 0.056 0.074		70	fruit	0.007	
Fresno, CA, USA, 1981[1,2]	EC	3	0.025 0.025 0.025		15	fruit	<0.002	NH 21 DHF81-6
	SC	3	0.05 0.05 0.05		15	fruit	0.008	
Fresno, CA, USA, 1981[1,2]	SC	3	0.05 0.05 0.05		119	fruit	<0.002	NH 21 LGT81-7
	EC	3	0.05 0.05 0.05		119	fruit	0.03	
Grandview, WA, USA, 1982[1,2]	EC	3	0.026		106	fruit	0.002	NH 17 82WA3
						juice/wine	<0.002	
						wet pomace	0.008	
						dried pomace	0.030	
Grandview, WA, USA, 1982[1,2]	EC	3	0.035		106	fruit	0.004	NH 17 82WA3
						juice/wine	<0.002	
						wet pomace	0.012	
						dried pomace	0.047	
Paw Paw, MI, USA, 1982[1,2]	EC	3	0.018 0.026 0.035		50	fruit	<0.002	NH 17 DE-082-31
						juice/wine	<0.002	
						wet pomace	0.003	
						dried pomace	0.012	
Paicines, CA, USA, 1983[1,2,5]	EC	2	0.044		94	fruit	0.006	NH 17 DF-83-62
						juice/wine	<0.002	
						wet pomace	0.011	
					94	fruit	0.005	
						juice/wine	<0.002	
						wet pomace	0.006	
					96	fruit	0.005	
						juice/wine	<0.002	
						wet pomace	0.005	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					96	fruit	0.006	
						juice/wine	<0.002	
						wet pomace	0.007	
Thermal, CA, USA, 1983[1,2,5]	EC	3	0.026 0.035 0.052		40	fruit	0.005	
						juice/wine	<0.002	
Thermal, CA, USA, 1983[1,2]	EC	3	0.026 0.035 0.052		40	fruit	0.005	NH 17 DHF-83-16
						juice/wine	<0.002	
						fruit	0.008	
		2	0.035 0.044		40	fruit	0.001	
Thermal, CA, USA, 1983[1,2]	EC	3	0.026 0.035 0.052		32	fruit	0.006	NH 17 DHF-83-17
	EC	3	0.026 0.035 0.052		32	fruit	0.007	
	SC	3	0.035 0.044 0.061		32	fruit	0.009	
Thermal, CA, USA, 1983[1,2]	EC	3	0.026 0.035 0.052		32	fruit	0.007	NH 17 DHF-83-18
	EC	3	0.026 0.035 0.052		32	fruit	0.003	
	SC	3	0.035 0.044 0.061		32	fruit	0.010	
Thermal, CA, USA, 1984	EC	3	0.025+ 0.033+ 0.05		47	fruit	<0.001	NH 02
		3	0.025+ 0.033+ 0.05		27	fruit	0.001	
		3	0.025+ 0.033+ 0.05		0	fruit	0.33	
					3	fruit	0.18	
					7	fruit	0.072	
					15	fruit	0.033	
					30	fruit	0.005	
Biola, CA, USA, 1984[1]	EC	2	0.033 0.05		82	fruit	0.004	NH 02 845-A
						juice	0.006	
						pomace	0.47	
						raisins	0.005	
						raisin waste	0.34	
Biola, CA, USA, 1984[1]	EC	3	0.025 0.033		82	fruit	0.004	NH 02 845-B

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
			0.05					
						juice	0.006	
						pomace	0.071	
						raisins	0.005	
						raisin waste	0.31	
Sanger, CA, USA, 1984[1]	EC	2	0.033 0.05	0.007 0.0107	86	fruit	0.006	NH 02 846-A
						juice	0.022	
						pomace	0.042	
						raisins	0.011	
						raisin waste	0.29	
Sanger, CA, USA, 1984[1,5]	EC	3	0.025 0.033 0.05	0.0053 0.007 0.0107	86	fruit	0.004	NH 02 846-B
						juice	0.008	
						pomace	0.035	
						raisins	0.004	
						raisin waste	0.52	
Biola, CA, USA, 1984[1]	EC	2	0.033 0.05	0.007 0.0107	92	fruit	0.004	NH 02 847-A
						juice	0.003	
						pomace	0.052	
Biola, CA, USA, 1984[1]	EC	3	0.025 0.033 0.05	0.0053 0.007 0.0107	92	fruit	0.003	NH 02 847-B
						juice	0.001	
						pomace	0.026	
Fresno, CA, USA, 1987	EC	4	0.025+ 0.033+ 0.05+ 0.05	0.0053+ 0.0071+ 0.0106+ 0.0106	30	fruit	<u>0.03</u>	NH 01
						juice	0.08	
						pomace	0.21	
		4	0.025+ 0.033+ 0.05+ 0.05	0.0053+ 0.0071+ 0.0106+ 0.0106	30	fruit	<u>0.02</u>	NH 01
						juice	0.07	
						pomace	0.19	
						raisin waste	0.48	
						raisins	0.04	
Biola, CA, USA, 1987[1]	EC	4	0.025 0.033 0.05 0.05	0.0053 0.0071 0.0106 0.0106	30	fruit	<u>0.026</u>	NH 01 87-13
						raisins	0.04	
						raisin waste	0.30	
Kerman, CA, USA, 1987[1]	EC	4	0.025 0.033 0.05 0.05		30	fruit	<u>0.019</u>	NH 01 87-14

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
						juice	0.047	
						pomace	0.09	
						raisins	0.04	
						raisin waste	0.26	
Bethlehem, PA, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	0.042	NH 20 8804R
Phelps, NY, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	0.006	NH 20 88060
Dundee, NY, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	0.010	NH 20 88061
Sunnyside, WA, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	0.033	NH 20 BJB88-05
Sunnyside, WA, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	0.017	NH 20 BJB88-06
Fresno, CA, USA, 1988	EC	3	0.025 0.033 0.050		30	fruit	0.007	NH 20 LE388-17
Biola, CA, USA, 1993[1,2]	EC	3	0.026 0.035 0.052		13	fruit	0.04	NH 17 DHF-83-56
					21	fruit	0.03	
					28	fruit	0.016	
					45	fruit	0.009	
					61	fruit	0.01	
					13	juice	0.018	
					21	juice	0.011	
					28	juice	0.014	
					45	juice	0.012	
					61	juice	0.008	
					13	wet pomace	0.037	
					21	wet pomace	0.021	
					28	wet pomace	0.028	
					45	wet pomace	0.015	
					61	wet pomace	0.016	
		4	0.026 0.035 0.052 0.052		13	fruit	0.005	
					21	fruit	0.039	
					28	fruit	0.032	
					45	fruit	0.015	
					61	fruit	0.017	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					13	juice	0.023	
					21	juice	0.013	
					28	juice	0.023	
					45	juice	0.016	
					61	juice	0.013	
					13	wet pomace	0.036	
					21	wet pomace	0.032	
					28	wet pomace	0.029	
					45	wet pomace	0.027	
					61	wet pomace	0.029	
Biola, CA, USA, 1993[1,2,5]	EC	3	0.026 0.035 0.052		14	fruit	0.023	NH 17 DHF-83-57
					21	fruit	0.024	
					28	fruit	0.019	
					45	fruit	0.021	
					59	fruit	0.009	
					14	juice	0.008	
					21	juice	0.012	
					28	juice	0.005	
					45	juice	0.003	
					59	juice	0.006	
					14	wet pomace	0.031	
					21	wet pomace	0.018	
					28	wet pomace	0.016	
					45	wet pomace	0.016	
					59	wet pomace	0.018	
					14	raisins	0.011	
					21	raisins	0.015	
					28	raisins	0.010	
					45	raisins	0.009	
					59	raisins	0.005	
					14	raisin waste	0.105	
					21	raisin waste	0.105	
					28	raisin waste	0.099	
					45	raisin waste	0.101	
					59	raisin waste	0.095	
		4	0.026 0.035 0.052 0.052		14	fruit	0.046	
					21	fruit	0.029	
					28	fruit	0.025	
					45	fruit	0.026	
					59	fruit	0.029	
					14	juice	0.008	
					21	juice	0.019	
					28	juice	0.008	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					45	juice	0.007	
					59	juice	0.009	
					14	wet pomace	0.027	
					21	wet pomace	0.026	
					28	wet pomace	0.027	
					45	wet pomace	0.019	
					59	wet pomace	0.019	
					14	raisins	0.017	
					21	raisins	0.019	
					28	raisins	0.014	
					45	raisins	0.010	
					59	raisins	0.012	
					14	raisin waste	0.171	
					21	raisin waste	0.191	
					28	raisin waste	0.179	
					45	raisin waste	0.131	
					59	raisin waste	0.206	
Sanger, CA, USA, 1993[1,2]	EC	4	0.026 0.035 0.052 0.052		16	fruit	0.053	NH 17 DHF-83-58
					21	fruit	0.053	
					30	fruit	0.043	
					48	fruit	0.081	
					63	fruit	0.032	
					16	raisin waste	0.347	
					21	raisin waste	0.401	
					30	raisin waste	0.216	
					48	raisin waste	0.332	
					63	raisin waste	0.271	
					16	juice	0.022	
					21	juice	0.025	
					30	juice	0.009	
					48	juice	0.017	
					63	juice	0.014	
					16	wet pomace	0.04	
					21	wet pomace	0.04	
					30	wet pomace	0.037	
					48	wet pomace	0.06	
					63	wet pomace	0.044	
					16	raisins	0.026	
					21	raisins	0.021	
					30	raisins	0.016	
					48	raisins	0.020	
					63	raisins	0.014	
Sanger, CA, USA, 1993[1,2]	EC	3	0.026 0.035 0.052		16	fruit	0.023	NH 17 DHF-83-58

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					21	fruit	0.024	
					30	fruit	0.016	
					48	fruit	0.024	
					63	fruit	0.024	
					16	raisin waste	0.178	
					21	raisin waste	0.157	
					30	raisin waste	0.111	
					48	raisin waste	0.177	
					63	raisin waste	0.124	
					16	juice	0.021	
					21	juice	0.019	
					30	juice	0.016	
					48	juice	0.015	
					63	juice	0.006	
					16	wet pomace	0.067	
					21	wet pomace	0.023	
					30	wet pomace	0.052	
					48	wet pomace	0.045	
					63	wet pomace	0.024	
					16	raisins	0.009	
					21	raisins	0.007	
					30	raisins	0.011	
					48	raisins	0.007	
					63	raisins	0.009	
Biola, CA, USA, 1993[1,2,5]	SC	3	0.035 0.052 0.061		14	fruit	0.024	NH 17 DHF-83-57
					21	fruit	0.028	
					28	fruit	0.040	
					45	fruit	0.020	
					59	fruit	0.009	
					14	juice	0.036	
					21	juice	0.023	
					28	juice	0.027	
					45	juice	0.014	
					59	juice	0.014	
					14	wet pomace	0.042	
					21	wet pomace	0.023	
					28	wet pomace	0.035	
					45	wet pomace	0.023	
					59	wet pomace	0.035	
					14	raisins	0.020	
					21	raisins	0.019	
					28	raisins	0.013	
					45	raisins	0.012	
					59	raisins	0.012	
					14	raisin waste	0.242	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					21	raisin waste	0.195	
					28	raisin waste	0.174	
					45	raisin waste	0.152	
					59	raisin waste	0.163	
Biola, CA, USA, 1993[1,2,5]	SC	4	0.035 0.052 0.061 0.070		14	fruit	0.068	NH 17
					21	fruit	0.052	
					28	fruit	0.044	
					45	fruit	0.040	
					59	fruit	0.044	
					14	juice	0.037	
					21	juice	0.038	
					28	juice	0.050	
					45	juice	0.021	
					59	juice	0.021	
					14	wet pomace	0.050	
					21	wet pomace	0.033	
					28	wet pomace	0.067	
					45	wet pomace	0.047	
					59	wet pomace	0.038	
					14	raisins	0.042	
					21	raisins	0.050	
					28	raisins	0.026	
					45	raisins	0.023	
					59	raisins	0.022	
					14	raisin waste	0.330	
					21	raisin waste	0.406	
					28	raisin waste	0.361	
					45	raisin waste	0.284	
					59	raisin waste	0.290	
Biola, CA, USA, 1993[1,2]	SC	3	0.035 0.052 0.061		13	fruit	0.061	NH 17 DHF-83-56
					21	fruit	0.024	
					28	fruit	0.029	
					45	fruit	0.041	
					61	fruit	0.019	
					13	juice	0.044	
					21	juice	0.015	
					28	juice	0.027	
					45	juice	0.028	
					61	juice	0.023	
					13	wet pomace	0.039	
					21	wet pomace	0.033	
					28	wet pomace	0.031	
					45	wet pomace	0.030	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					61	wet pomace	0.028	
Biola, CA, USA, 1993[1,2]	SC	4	0.035 0.052 0.061 0.070		13	fruit	0.061	NH 17 DHF-83-56
					21	fruit	0.038	
					28	fruit	0.053	
					45	fruit	0.060	
					61	fruit	0.039	
					13	juice	0.043	
					21	juice	0.032	
					28	juice	0.094	
					45	juice	0.064	
					61	juice	0.053	
					13	wet pomace	0.052	
					21	wet pomace	0.037	
					28	wet pomace	0.053	
					45	wet pomace	0.055	
					61	wet pomace	0.057	
Sanger, CA, USA, 1993[1,2]	SC	3	0.035 0.052 0.061		16	fruit	0.067	NH 17 DHF-83-58
					21	fruit	0.032	
					30	fruit	0.061	
					48	fruit	0.061	
					63	fruit	0.021	
					16	juice	0.040	
					21	juice	0.039	
					30	juice	0.032	
					48	juice	0.031	
					63	juice	0.016	
					16	wet pomace	0.048	
					21	wet pomace	0.042	
					30	wet pomace	0.030	
					48	wet pomace	0.036	
					63	wet pomace	0.041	
					16	raisins	0.024	
					21	raisins	0.050	
					30	raisins	0.019	
					48	raisins	0.015	
					63	raisins	0.012	
					16	raisin waste	0.384	
					21	raisin waste	0.492	
					30	raisin waste	0.337	
					48	raisin waste	0.362	
					63	raisin waste	0.312	
Sanger, CA, USA, 1993[1,2]	SC	4	0.035 0.052		16	fruit	0.100	NH 17 DHF-83-58

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
			0.061 0.070					
					21	fruit	0.053	
					30	fruit	0.085	
					48	fruit	0.060	
					63	fruit	0.034	
					16	juice	0.076	
					21	juice	0.034	
					30	juice	0.045	
					48	juice	0.044	
					63	juice	0.034	
					16	wet pomace	0.053	
					21	wet pomace	0.039	
					30	wet pomace	0.049	
					48	wet pomace	0.051	
					63	wet pomace	0.046	
					16	raisins	0.064	
					21	raisins	0.059	
					30	raisins	0.034	
					48	raisins	0.036	
					63	raisins	0.042	
					16	raisin waste	1.18	
					21	raisin waste	0.88	
					30	raisin waste	0.74	
					48	raisin waste	1.07	
					63	raisin waste	0.62	

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in Australia

[1] No weather data submitted

[2] Duration of sample storage unspecified (Californian trials: 11 months maximum by calculation)

[3] NH23 F/H01/85 samples stored for 15 months

[4] No example chromatograms submitted

[5] Some high associated recoveries (NH 02 fruit, 122%; DHF 83-57 pomace, 123%, 136%; DHF 83-62 pomace 125%), but mean recoveries acceptable

[6] No detailed report submitted

[7] No English translation provided

Strawberries. GAP was reported for Denmark, Ireland, Italy, Japan (indoor and outdoor), The Netherlands, Spain and the UK. The maximum application rates are 0.03-0.084 kg ai/ha with PHIs of 1-14 days.

Data were available from Italy, Japan, Spain and The Netherlands. Two Italian trials and one Spanish trial were according to Italian GAP (0.048 kg ai/hl, 7-day PHI), with residues of 0.12-0.18 mg/kg. Spanish GAP has a PHI of 3 days (0.0048 kg ai/hl) and was only represented by the single Spanish trial with a residue of 0.25 mg/kg. at 3 days. Three Dutch trials were according to GAP (0.084 kg ai/ha, treatment before flowering) with residues of <0.01-0.02 mg/kg, but all the Dutch trials were submitted in summary form only. Japanese indoor GAP (0.003 kg ai/hl, 1-day PHI) was represented by 7 trials in which the crops were all protected by what was described as "vinyl housing cultivation with plastic mulch on bed". Residue levels in the trials were 0.04-0.56 mg/kg in samples taken 1 day after the final treatment.

Raspberries. Information on GAP was reported for Ireland and the UK. The application rate is 0.04 kg ai/ha with a PHI of 14 days. Only one trial was available from the UK, and this was at an exaggerated application rate.

Table 31. Supervised residue trials on strawberries and raspberries.

Location, year	Application					PHI, days	Residues, mg/kg	Ref.
	Sample	Form	No.	kg ai/ha	kg ai/hl			
STRAWBERRY								
Grosseto, Italy, 1979[1,2,3,5]	Field	WP	3	0.042	0.0042	7	0.12	NC 11
						16	0.09	
						22	0.07	
Grosseto, Italy, 1979[1,2,3,5]	Field	WP	3	0.042	0.0042	7	0.14	NC 12
						16	0.10	
						22	0.05	
Nara Pref., Japan, 1984[1,3]	Protected	WP	3	0.045	0.003	1	0.32**	NC16
						3	0.17	
						8	0.29	
Chiba Pref., Japan, 1984[1,3]	Protected	WP	3	0.045	0.003	1	0.43**	NC 16
						3	0.48	
						6	0.44	
Saitama Pref, Japan, 1987[1,3]	Protected	WP	3	0.06	0.003	1	0.04**	NC 16
Wakayama, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.13**	NC 16
Hyogo, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.56**	NC 16
Osaka, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.20**	NC 16
Shiga Pref, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.21**	NC 16
Ophensden, Netherlands, 1979[6]	Field	EC	1	0.084		238	0.02	6
Zaltbommel, Netherlands, 1979[6]	Field	EC	1	0.084		239	<0.01	6
Zundert, Netherlands, 1979[6]	Field	EC	1	0.084		238	<0.01	6
Breda, Netherlands, 1982[6]	Field	EC	1	0.07		15	<0.01	6
Vilanova de Castello, Spain, 1986[1,3,4,7]	Field	EC	3	0.096	0.0048	0	0.3	13
						3	0.25*	
						7	0.18	
						14	0.1	
						21	0.07	
RASPBERRY								
Earl Wood, Windlesham, UK, 1994[1,2,4]	Field	SC	3	0.075	0.0036	11	0.05	ND 01

Underlined residues are from treatments according to GAP in Italy; those underlined twice from treatments according to GAP in The Netherlands

* According to GAP in Spain
** According to Japanese indoor GAP
[1] No weather data submitted
[2] Method of analysis unspecified
[3] No example chromatograms submitted
[4] Duration of sample storage unspecified
[5] Crop variety unspecified
[6] No detailed report submitted
[7] No English translation provided

Bananas. GAP was reported for Honduras and Nicaragua. The application rates in both countries are 0.08-0.12 kg ai/ha with a PHI of 0 days.

Data were available from Ecuador, Costa Rica, Honduras and the Philippines. In all trials a low-volume application (20-48 l/ha) was made using a motorized backpack sprayer. Six trials reflected the use in Honduras and Nicaragua with residues 0 or 1 day after the final treatment of <0.01-0.19 mg/kg in unbagged bananas and <0.01-0.12 mg/kg in bagged bananas. Six further trials at twice the maximum application rate (i.e. 0.24 kg ai/ha) were also available with residues of 0.03-0.3 mg/kg in unbagged bananas and <0.01-0.12 mg/kg in bagged bananas.

Table 32. Supervised residue trials on bananas in 1992. All with 7 applications of EC.

Location, year	Application		Sample	Bagged/Un-bagged	PHI, days	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl					
Limon, Costa Rica -East	0.12	0.55	whole	unbagged	0	0.02	NL 02
			pulp	unbagged	0	0.02	
			whole	unbagged	1	0.02	
			pulp	unbagged	1	0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Limon, Costa Rica -East	0.24	1.1	whole	unbagged	0	0.03	NL 02
			pulp	unbagged	0	0.03	
			whole	unbagged	1	0.03	
			pulp	unbagged	1	0.05	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	0.01	
			pulp	bagged	1	<0.01	
Limon, Costa Rica -West	control		whole	bagged	-	<0.01 0.01	NL 02
	0.12	0.55	whole	unbagged	0	0.03	
			pulp	unbagged	0	0.01	
			whole	unbagged	1	0.03	
			pulp	unbagged	1	<0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Limon, Costa Rica -West	control	control	whole	bagged	-	<0.01 0.01	NL 02

Location, year	Application		Sample	Bagged/Un-bagged	PHI, days	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl					
	0.24	1.1	whole	unbagged	0	0.05	
			pulp	unbagged	0	-	
			whole	unbagged	1	0.05	
			pulp	unbagged	1	0.01	
			whole	bagged	0	0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Guayas, Ecuador Site 1	0.12	0.6	whole	unbagged	0	0.09	NL 02
			pulp	unbagged	0	0.05	
			whole	unbagged	1	0.19	
			pulp	unbagged	1	0.02	
			whole	bagged	0	0.12	
			pulp	bagged	0	0.01	
			whole	bagged	1	0.02	
			pulp	bagged	1	0.12	
Guayas, Ecuador Site 1	0.24	1.2	whole	unbagged	0	0.25	NL 02
			pulp	unbagged	0	0.12	
			whole	unbagged	1	0.22	
			pulp	unbagged	1	0.11	
			whole	bagged	0	0.02	
			pulp	bagged	0	0.01	
			whole	bagged	1	0.03	
			pulp	bagged	1	0.01	
Guayas, Ecuador Site 2	0.12	0.6	whole	unbagged	0	0.12	NL 02
			pulp	unbagged	0	0.11	
			whole	unbagged	1	0.16	
			pulp	unbagged	1	0.04	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	0.01	
			pulp	bagged	1	0.02	
Guayas, Ecuador Site 2	0.24	1.2	whole	unbagged	0	0.05	NL 02
			pulp	unbagged	0	0.07	
			whole	unbagged	1	0.3	
			pulp	unbagged	1	0.12	
			whole	bagged	0	0.04	
			pulp	bagged	0	0.03	
			whole	bagged	1	0.04	
			pulp	bagged	1	0.04	
La Lima, Honduras Site 1	0.12	0.00025	whole	unbagged	0	0.01	NL 02
			pulp	unbagged	0	<0.01	
			whole	unbagged	1	<0.01	
			pulp	unbagged	1	<0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	

Location, year	Application		Sample	Bagged/Un-bagged	PHI, days	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl					
			pulp	bagged	1	<0.01	
La Lima, Honduras Site 1	0.24	0.5	whole	unbagged	0	0.02	NL 02
			pulp	unbagged	0	0.02	
			whole	unbagged	1	0.02	
			pulp	unbagged	1	0.02	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
La Lima, Honduras Site 2	0.12	0.25	whole	unbagged	0	<0.01	NL 02
			pulp	unbagged	0	<0.01	
			whole	unbagged	1	0.01	
			pulp	unbagged	1	0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	ND	
			whole	bagged	1	<0.01	
			pulp	bagged	1	ND	
La Lima, Honduras -Site 2	0.24	0.5	whole	unbagged	0	0.02	NL 02
			pulp	unbagged	0	<0.01	
			whole	unbagged	1	0.02	
			pulp	unbagged	1	0.02	
			whole	bagged	0	<0.01	
			pulp	bagged	0	0.02	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Philippines[1]	0.15	0.11	pulp	NR	8	0.02	NL 03
			peel	NR	8	0.07	
			whole	NR	8	0.04	

Underlined residues are from treatments according to GAP in Honduras and Nicaragua
ND none detected
NR not recorded
[1] 1991

Cucumbers. GAP was reported for Brazil, Denmark, Ireland, Japan, The Netherlands, Uruguay and the UK. Several other countries reported GAP for the group "cucurbits". The maximum application rates are 0.019-0.072 kg ai/ha or 0.0012-0.0072 kg ai/hl with PHIs of 1-7 days.

Residue trials data were available from Austria, Italy, Brazil and the UK. One trial with a residue of 0.03 mg /kg was according to UK and Irish GAP (0.002 kg ai/hl, 2-day PHI) and a Brazilian trial with a residue at 4 days of 0.003 mg/kg complied with GAP in Uruguay. Residues in the Italian trials were at PHIs of 10-15 days, although this is longer than any reported GAP. There were no results at the Japanese GAP PHI of 1 day.

Gherkins. GAP was reported for The Netherlands (0.0024 kg ai/hl, 3-day PHI) for both protected and field use. Other countries had GAP for the group "cucurbits".

Two replicated Dutch trials were submitted in summary form in which a high application concentration of 0.24 kg ai/hl was reported, with the rate per hectare unspecified. Residues in samples taken 3 days after the final treatment were 0.02-0.06 mg/kg.

Table 33. Supervised residue trials on cucumbers and gherkins.

Location, year	Field protected	Application				PHI, days	Residues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
CUCUMBER								
Tadten, Austria, 1976[1,2,3,5]	Field	EC	1	0.012	0.0006	2	0.03	NB 01
		EC	1	0.024	0.0012	2	0.02	
Campinas, Brazil, 1986[1,3-5]	Field	EC	3	0.018		4	0.003	NB 29
			3	0.036		4	0.01	
Bellaria, Italy, 1977 [1-5]	Field	WP	8		0.003 high vol.	10	<0.01	NB 08
Borghesi, Italy, 1977 [1-5]	Field	WP	7		0.003 high vol.	22	<0.01	NB 09
Parma, Italy, 1981[1-3]	Field	SC	1	0.024	0.0024	15	<0.01	NB 15
Windlesham, Surrey, UK, 1976[1-3]	Protected	EC	6	250 ml/plant	0.002	2	0.03	NB 04
						4	0.05	
			6	250 ml/plant	0.004	2	0.09	
						4	0.07	
			6	250 ml/plant	0.008	2	0.03	
						4	0.16	
GHERKINS								
Denne, Netherlands, 1977[7]	Field?	EC	1		0.24	1	0.1	6
						3	0.03	
			1		0.24	1	0.07	
							0.05	
							0.1	
							0.08	
						3	0.06	
							0.03	

fenarimol

Location, year	Field protected	Application				PHI, days	Residues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
							0.05	
							0.02	
Wernhout, Netherlands, 1977[7]	Field?	EC	1		0.24	1	0.08	6
							0.06	
							0.1	
							0.05	
						3	0.06	
							0.04	
							0.03	
							0.02	

Underlined residues are from treatments according to GAP in UK and Ireland; those underlined twice from treatments according to GAP in Uruguay
[1] No weather data provided
[2] Method of analysis unspecified
[3] No example chromatograms submitted
[4] Duration of sample storage unspecified
[5] Crop variety unspecified
[6] No English translation provided
[7] No detailed report submitted

Melons (including cantaloupes) and watermelons. Indoor GAP for melons was reported for The Netherlands (0.0024 kg ai/hl, 3-day PHI), and outdoor GAP for melons for Japan, Portugal and Brazil and for watermelons for Japan, Brazil and Uruguay, as well as GAP for "cucurbits" in other countries. The maximum application rates are 0.012-0.036 kg ai/ha with PHIs of 1-7 days.

The only relevant indoor data were from two Spanish trials on melons but these were with a higher spray concentration than in Dutch GAP.

Outdoor trials were carried out on melons in France, Italy, Brazil and Spain, on watermelons in Italy and Brazil and on cantaloupes in Italy. In four French trials according to Greek GAP for cucurbits (0.024 kg ai/ha, 1-day PHI) residues were <0.01 and <0.01-0.11 mg/kg in the pulp and peel, respectively, 2 days after the final treatment. Residues at 4 days were <0.01 and 0.01-0.07 mg/kg in the pulp and peel respectively. When a double rate was applied (0.048 kg ai/ha) residues were only <0.01-0.02 and 0.04-0.09 mg/kg in the pulp and peel at 2 days. In these French trials the actual weights of pulp and peel were not recorded.

A number of other trials on melons in Brazil, Italy and Spain were at higher application rates than GAP at 0.036-0.048 kg ai/ha but residues were low (0.01-0.04 mg/kg) at 3-4 days. In a further three outdoor trials on watermelons in Italy and Brazil and two Italian trials on cantaloupes residues were all below the LOD (<0.01 mg/kg or ND) 4-14 days after the final treatment. Brazilian GAP (0.024 kg ai/ha, 4-day PHI) was represented by two trials; residues were 0.005 mg/kg in melons and "not detected" in watermelons, but in both trials the duration of sample storage was unspecified.

Table 34. Supervised residue trials on melons, watermelons and canteloupe melons.

Location, year	Field/ protected	Application				PHI, days	Sample	Residues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl				

Location, year	Field/ protected	Application				PHI, days	Sample	Res-idues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl				
MELON									
Campinas, Brazil, 1986[1,4-6]	Field	EC	3	0.018		4	whole	0.005	NB 29
			3	0.036		4	whole	0.04	
Savonieries, France, 1976[1,2,4]	Field	EC	3	0.01	0.0017	10	whole	<0.01	NB 02
			3	0.015	0.0025	10	whole	<0.01	
St Nicholas, France, 1980[1,2,4]		EC	1	0.024	0.0024	0	pulp	<0.01	NB 20
						0	pulp	<0.01	
						2	peel	0.03	
						2	peel	0.11	
						4	peel	0.06	
						4	peel	0.04	
Moissac, France, 1980 [1,2,4]	Field	EC	1	0.024	0.0025	0	pulp	<0.01	NB 21
						0	peel	0.09	
						2	pulp	<0.01	
						2	peel	0.03	
						4	pulp	<0.01	
						4	peel	0.01	
			1	0.048	0.0048	0	pulp	<0.01	
						0	peel	0.08	
						2	pulp	<0.01	
						2	peel	0.04	
						4	pulp	<0.01	
						4	peel	0.04	
St Nicola de la Grave, France, 1980[1,2,4]	Field	EC	1	0.024	0.0024	0	pulp	<0.01	NB 22
						0	peel	0.19	
						2	pulp	<0.01	
						2	peel	0.09	
						4	pulp	<0.01	
						4	peel	0.07	
			1	0.048	0.0048	0	pulp	0.01	
						0	peel	0.22	
						2	pulp	<0.01	
						2	peel	0.09	
						4	pulp	0.01	
						4	peel	0.08	
Moissac, France, 1980[1,2,4]	Field	EC	1	0.024	0.0022	0	pulp	<0.01	NB 23
						0	peel	<0.01	
						2	pulp	<0.01	
						2	peel	<0.01	
						4	pulp	<0.01	
						4	peel	0.04	
			1	0.048	0.0048	0	pulp	0.02	
						0	peel	013	
						2	pulp	0.02	
						2	peel	0.07	

Location, year	Field/ protected	Application				PHI, days	Sample	Res-idues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl				
						4	pulp	<0.01	
						4	peel	0.04	
Volania, Ferrara, Italy, 1994	Field	SC	3	0.018+ 0.018+ 0.036	0.0036	7	peel	0.01	NB 32
						7	pulp	ND	
						7	whole	<0.01	
			3	0.024+ 0.024+ 0.048	0.0048	7	peel	0.01	
						7	pulp	ND	
						7	whole	<0.01	
Gavello, Italy, 1994	Field	SC	3	0.018+ 0.018+ 0.036	0.0036	7	peel	0.03	NB 32
						7	pulp	ND	
						7	whole	0.01	
			3	0.024+ 0.024+ 0.048	0.0048	7	peel	0.02	
						7	pulp	ND	
						7	whole	<0.01	
Los Alcazares, Spain, 1994	Protected	SC	3	0.037	0.0048	-1	whole	<0.01	NB 31
						0	whole	0.02	
						3	whole	0.02	
						5	whole	0.02	
						7	whole	<0.01	
Sevilla, Spain, 1994	Protected	SC	3	0.048	0.0048	-1	whole	<0.01	NB 31
						0	whole	0.01	
						3	whole	0.01	
						5	whole	<0.01	
						7	whole	0.01	
Romani, Spain, 1986[1,2,4,5,7]	Field	EC	2	0.096	0.0048	0	whole	0.1	13
						4	whole	0.07	
						7	whole	0.02	
						14	whole	ND	
CANTALOUPE MELONS									
Parma, Italy, 1977[1-6]	Field	WP	1	0.012	0.003	10	whole	<0.01	NB 11
Parma, Italy, 1981[1,2,4]	Field	SC	3	0.024	0.0024	14	whole	<0.01	NB 24
WATERMELONS									
Parma, Italy, 1976[1,2,4]	Field	EC	3	0.020	0.002	11	whole	<0.01	NB 03
Parma, Italy, 1977[1-4]	Field	WP	3		0.0018+ 0.0024+ 0.003	10	whole	<0.01	NB 12
Campinas, Brazil, 1986[1,4,6]	Field	EC	4	0.018	not reported	4	whole	ND	NB 29
			4	0.036	not reported	4	whole	ND	

Underlined residues are from treatments according to GAP in Greece; those underlined twice from treatments according to GAP in Brazil.

ND - not detected
[1] No weather data submitted
[2] Method of analysis unspecified
[3] Low associated recoveries (65% for cantaloupe trial, 68% for watermelon trial)
[4] No example chromatograms submitted
[5] Duration of sample storage unspecified
[6] Crop variety unspecified
[7] No English tranlation provided

Pumpkins, courgettes and squashes. GAP was reported for pumpkins for The Netherlands (indoor only), Brazil, Japan and Peru, for squash for Argentina (summer) and Uruguay, for courgettes for The Netherlands, and for "cucurbits" in other countries. The maximum application rates are 0.012-0.06 kg ai/ha with PHIs of 1-7days.

No data on indoor trials were submitted. One trial on squash in Brazil, complying with GAP for Argentina and Uruguay (0.024 kg ai/ha, 4 days PHI), showed a residue of 0.005 mg/kg. One Australian replicated trial on zucchini courgettes and one on pumpkins accorded with Australian GAP for curcurbits (0.024 kg ai/ha, 3-day PHI). Residues were very low; 0.001-0.01 mg/kg three days after the final treatment. The duration of laboratory sample storage was not given in the Australian trials considered to be according to GAP.

Table 35. Supervised residue trials on squash, zucchini, courgettes and pumpkins (whole commodities analysed).

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
SQUASH							
Campinas, Brazil, 1986[1,4,6]	EC	4	0.018	not reported	4	0.005	NB 29
		4	0.036	not reported	4	0.008	
Parma, Italy, 1977[1,2,3-6]	WP	3	0.12	0.003	15	<0.01	NB 10
Parma, Italy, 1981[1,2,4]	WP	4	0.024	0.0024	15	<0.01	NB 26
ZUCCHINI COURGETTES							
Pokolbin, NSW, Australia, 1985[1,5,6]			control	control	-	0.005	NB 30
	EC	4	0.01	not reported	3	0.01	
		4	0.02	not reported	3	0.01	
		4	0.03	not reported	3	0.02	
PUMPKINS							
Pokolbin, NSW, Australia, 1985[1,5,6]			control	control	-	0.001	NB 30
	EC	4	0.01	not reported	3	0.001	
		4	0.02	not reported	3	0.003	
		4	0.03	not reported	3	0.001	

Underlined residues are from treatments according to GAP for squash in Argentina and Uruguay; those underlined twice from treatments according to GAP for cucurbits in Australia
[1] No weather data provided
[2] Method of analysis unspecified
[3] Low associated recoveries (69%)
[4] No chromatograms submitted
[5] Duration of sample storage unspecified
[6] Crop variety unspecified

Tomatoes. GAP was reported for Denmark (glasshouse and field use), Italy, Japan, The Netherlands (glasshouse and field use), Spain and the UK. The maximum application rates are 0.036-0.072 kg ai/ha or 0.002-0.0048 kg ai/hl with PHIs of 1-7days.

Data were available from Italy, Spain, The Netherlands and Greece. Treatments in two Netherlands indoor trials were comparable to Danish GAP (0.036 kg ai/ha or 0.0048 kg ai/hl, 2-day PHI). Residues in both were 0.03 mg/kg at 2 days. Italian GAP (0.0048 kg ai/hl, 7-day PHI) and Spanish GAP (0.006 kg ai/hl, 7-day PHI) were reflected in one Spanish and two Italian trials with residues of 0.03, 0.03 and 0.05 mg/kg at 7days.

Peppers. GAP for peppers is the same as for tomatoes except that Denmark has no registered use.

Trials data were available from Italy, Spain and Israel. Spanish and Italian GAP (0.0048 or 0.006 kg ai/hl with a PHI of 7days) were represented by 6 trials in Italy and Spain. Residues were 0.03-0.07 mg/kg and 0.07-0.5 mg/kg respectively in samples taken 7 days after the final treatment. The duration of sample storage was not specified in the Spanish trials.

Egg plants (aubergines). Outdoor GAP was reported for Italy and Japan. The maximum application rates are about 0.04 kg ai/ha or about 0.002-0.0048 kg ai/hl with a PHI of 1 day in Japan and 7 days in Italy.

Only one Italian trial was reported, in which the residue was <0.01 mg/kg 15 days after harvest.

Table 36. Supervised residue trials on tomatoes, peppers and egg plants.

Location, year	Field/ protected	Application				PHI, days	Res, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
TOMATOES								
Thessaloniki, Greece, 1994	Protected	EC	3	0.026 2 x 0.048	3 x 0.004	31	0.03	NE 12 GHE-P-4012
Grosetto, Italy, 1979[1-3]	Field	WP	3	0.084	0.0042	7	0.03	NE 03 I79-251
						14	0.06	
						21	<0.01	
Grosetto, Italy, 1979[1-3,5]	Field	WP	3	0.084	0.0042	7	0.03	NE 07 I79-250
						14	<0.01	
						21	<0.01	
Parma, Italy, 1981[1-3]	Field	SC	3	0.048	0.0042-0.0048	15	<0.01	NE 09 I81-258
Huissen, Netherlands, 1994	Protected	SC	3	0.048	0.0024	0	0.04	NE 11 R94-062-01
						1	0.04	
						2	0.03	
						3	0.03	
Bemmel, Netherlands, 1994	Protected	SC	3	0.048	0.0024	0	0.03	NE 11 R94-062-02
						1	0.03	
						2	0.03	
						3	0.02	
Marzarron, Spain, 1993[1]	Field	EC	3	*c.*0.06-0.08	0.0048	0	0.08	NE 08 GHE-P-3653
						2	0.06	
						7	0.05	
PEPPERS								

Location, year	Field/ protected	Application				PHI, days	Res, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
Yad Natan, Israel, 1977[1-3]	Field	EC	2	0.036		30	0.03	NE 04 ISL79-2
						16	0.04	
						14	0.04	
						7	0.08	
						0	0.13	
			2	0.072		30	0.02	
						16	0.03	
						14	0.09	
						7	0.01	
						0	0.32	
Grosetto, Italy, 1979[1-3]	Field	WP	3		0.0042	7	0.07	NE 05 I79-250
						14	0.12	
						21	0.02	
Grosetto, Italy, 1979[1-3]	Field	WP	3		0.0042	7	0.03	NE 06 I79-251
						14	0.01	
						21	0.03	
Parma, Italy, 1981[1-3]	Field	SC	3	0.048	0.0048	15	<0.01	NE 10 I81-259
Cartagena, Spain, 1977[1-3,7]	Field		3		0.0024	30	0.03	NE 02 E77-129
					0.003		0.03	
Benifaio, Spain, 1986[1,3,6,7]	Field	EC	3	0.108	0.006	0	0.3	Ref. 13
						4	0.15	
						7	0.07	
						14	ND	
						21	ND	
Sollana, Spain, 1987[1,3,4,6,7]	Field	EC	1	0.126	0.006	0	0.27	Ref. 13
						3	0.23	
						7	0.12	
						14	0.05	
						21	0.03	
Benifaio, Spain, 1992[1,3,4,6,7]	Field	EC	1	0.15	0.006	0	0.6	Ref. 13
						3	0.56	
						7	0.5	
						14	0.2	
						21	0.1	
Benifaio, Spain, 1993[1,3,4,6,7]	Field	EC	1	0.12	0.006	0	0.21	Ref. 13
						3	0.26	
						7	0.08	
						14	0.05	
						21	0.03	
EGG PLANTS (AUBERGINES)								
Parma, Italy, 1981[1-3,5]	Field	SC	3		0.008	15	<0.01	NB 27 I81-260

Underlined residues are from treatments according to GAP in Spain and Italy

[1] No weather data submitted

[2] Method of analysis unspecified

[3] No example chromatograms submitted

[4] Duration of sample storage unspecified
[5] Crop variety unspecified
[6] No English translation provided
[7] The meeting was informed that samples were analysed within 24 hours of receipt at the laboratory.

Beetroots and carrots. Only Dutch GAP for "vegetables" was reported (0.036 kg ai/ha or 0.0024 kg ai/hl, 3-day PHI). There was one Netherlands trial on each of these crops in which residues were <0.01-0.02 mg/kg in samples taken 27 days after treatment.

Table 37. Supervised residue trials on beetroots and carrots at Slootdorp, The Netherlands, in 1984. 2 x 0.06 kg ai/ha EC applied in both trials (No example chromatograms submitted and no English translation provided for either trial).

PHI, days	Sample	Residues, mg/kg	Ref.
27	Beetroots, whole, roots and soil removed	0.01	KVW267/CTB/PD
		0.01	
		0.01	
		0.02	
		0.02	
27	Carrots, whole, soil removed	<0.01	KVW268/CTB/PD
		<0.01	
		<0.01	
		<0.01	

Globe artichokes. GAP was reported only for Italy (0.0048 kg ai/hl or 0.038 kg ai/ha, 7-day PHI). Six Italian trials with residues of <0.01-0.06 mg/kg were considered to reflect GAP. In two of these (1979) the analytical recovery was low (61%). In a Spanish trial a higher residue of 0.26 mg/kg was found at 7 days, but a high volume of water (2,500 l/ha) was applied and the spray concentration was higher (0.006 kg ai/hl) than that registered in Italy.

Table 38. Supervised residue trials on globe artichokes.

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Grosseto, Italy, 1979[1,24,5,7]		2	0.084	0.0042	7	<0.01	NI 01
					14	<0.01	
					21	<0.01	
Grosseto, Italy, 1979[1,2,4,5]	WP	3	0.084	0.0042	7	0.03	NI 02
					14	<0.01	
					21	<0.01	
Grosseto, Italy, 1981[1,2,6]	SC	3	0.048	0.0048	14	0.03	NB 28
			control	control	-	0.02	
Del Gardinia, Italy, 1994	SC	3	0.035-0.036	0.0036	-1	0.04	NI 05
					1	0.07	
					7	0.04	
					14	<0.01	
					21	<0.01	
Del Gardinia, Italy, 1994	SC	3	0.046-0.048	0.0048	-1	0.03	NI 05

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					1	0.10	
					7	0.06	
					14	0.02	
					21	<0.01	
Sezze, Italy, 1994	SC	3	0.031-0.035	0.0036	-1	0.02	NI 05
					1	0.11	
					7	0.05	
					14	0.02	
					21	<0.01	
Sezze, Italy, 1994	SC	3	0.042-0.047	0.0048	-1	0.05	NI 05
					1	0.19	
					7	0.06	
					14	0.04	
					21	0.02	
L'Alcudia, Spain, 1987[1,6,8]	EC	1	0.153	0.006	0	0.42	Ref. 13
					3	0.33	
					7	0.26	
					14	0.14	
					21	0.09	

Underlined residues are from treatments according to GAP in Italy
[1] No weather data submitted
[2] Method of analysis unspecified
[3] No control plot data
[4] Crops stored for 19 months before analysis
[5] Low recoveries (61%)
[6] No example chromatograms submitted
[7] Crop variety not specified
[8] No English translation provided

Witloof chicory. Only Dutch GAP for "vegetables" was reported (0.036 kg ai/ha or 0.0024 kg ai/hl, 3-day PHI). In a single trial residues were <0.01 mg/kg in samples taken 60 days after harvest.

Table 39. Supervised residue trials on witloof chicory at Slootdorp, The Netherlands, in 1984. 2 x 0.06 kg ai/ha of EC. No example chromatograms submitted and no English translation provided.

Sample	PHI, days	Residues, mg/kg	Reference
Crop	60	<0.01	KVW266/CTB/PD
Roots, soil removed	60	<0.01	

Pecans. GAP was reported for the USA and Mexico. The maximum application rates are 0.098 and 0.108 kg ai/ha with a PHI of 30 days in the USA and pre-flowering application in Mexico.

Twelve trials were carried out in the USA in four of which (one replicated) the final applications (0.074-0.12 kg ai/ha) were comparable to the registered rate in the USA (0.098 kg ai/ha). Residues were <0.002 and <0.002-0.02 mg/kg in the kernels and shells respectively after 35-153 days. In a further series of trials in which an exaggerated application rate was used (0.15-0.32 kg ai/ha) residues were <0.002-0.02 and <0.002-0.16 in the kernels and shells in samples taken 17-55 days after treatment. In one of these trials the laboratory samples were stored for 11 months before analysis.

Table 40. Supervised residue trials (field) on pecans in the USA.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Byron, GA, 1981[1]	EC	10	0.148*	0.003	30	kernel	<0.002	NM 01
Albany, GA, 1981[1,2,3]	SC	14	0.197*		35-39	kernel	<0.002	NM 01 RBC 81-25
						shell	0.164	
	EC	14	0.197*		35-39	kernel	0.02	
					55	shell	0.155	
Byron, GA, 1982[1]	EC	9	0.158*		55	kernel	<0.002	NM 01 USDA
						shell	<0.002	
Albany, GA, 1982[1]	EC	17	0.149*		29	kernel	<0.002	NM 01 RBC 82-1
						shell	<0.002	
					43	kernel	<0.002	
						shell	<0.002	
Albany, GA, 1982[1]	EC	17	0.149*		17	kernel	<0.002	NM 01 RBC 1, 2-5
						shell	<0.002	
Fitzpatrick, AL, 1982[1]	EC	14	0.149*		43	kernel	<0.002	NM 01 RDH 82-3
						shell	0.01	
Blakely, GA, 1982[1]	EC	11	0.12		38	kernel	<0.002	NM 02 RBC 83-12
					84	kernel	<0.002	
					107	kernel	<0.002	
					155	kernel	<0.002	
			0.12		38	shell	<0.002	
					84	shell	<0.002	
					107	shell	<0.002	
					155	shell	<0.002	
Artesia, MS, 1983[1]	EC	6	0.14		124	kernel	<0.002	NM 02 MS UNI
						shell	0.008	
		6	0.094		124	kernel	<0.002	
						shell	0.002	
Albany, GA, 1983[1]	EC	5	0.14		171	kernel	<0.002	NM 02 RBC 83-15
						shell	<0.002	
			0.32*		171	kernel	<0.002	
						shell	<0.002	
Albany, GA, 1983[1]	EC	11	0.12		25	kernel	<0.002	NM 02 RBC 83-16
			0.08		71	kernel	<0.002	
			0.063		94	kernel	<0.002	
			0.045		142	kernel	<0.002	
			0.12		25	shell	<0.002	
			0.08		71	shell	<0.002	
			0.063		94	shell	<0.002	
			0.045		142	shell	<0.002	
Fitzpatrick, GA, 1983[1]	EC	7	0.074		153	kernel	<0.002	NM 02 RDH 83-10
			0.10			kernel	<0.002	
			0.14			kernel	<0.002	
			0.11			kernel	<0.002	
			0.074		153	shell	0.02	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
			0.10			shell	0.004	
			0.14			shell	0.007	
			0.11			shell	<0.002	
Montgomery, AL, 1983[1]	EC	7	0.074		136	kernel	<0.002	NM 02 RDH 83-11
			0.10			kernel	<0.002	
			0.14			kernel	<0.002	
			0.11			kernel	<0.002	
			0.074		136	shell	0.014	
			0.10			shell	0.013	
			0.14			shell	0.023	
			0.11			shell	<0.002	

Underlined results are according to the registered application rate in the USA but are at longer PHIs; those underlined twice are from treatments according to GAP in the USA including the PHI.
* exaggerated application rate
[1] No weather data submitted
[2] Crops stored for 11 months before analysis
[3] Low associated recoveries (shells 44%)

Hops. GAP was reported for Germany and Spain. The maximum application rate was either 0.06 kg ai/ha or 0.0015 kg ai/hl with a 10-day PHI in Germany and 0.0048 kg ai/hl with an unspecified PHIs in Spain.

Four trials in Germany were all conducted according to German GAP. Residues in dried hops harvested 10 days after the final treatment were 2.22-3.55 mg/kg. Samples were stored for 13 months before analysis. The results are shown in Table 41.

Table 41. Supervised residue trials on hops, beer and spent yeast in Germany, 1990. All trials with 4 x 0.06 kg ai/ha (0.0015 kg ai/hl) of WP.

Location, year	PHI, days	Sample	Residues, mg/kg	Ref.
Rohr[1,2]	10	fresh hops	0.65	NJ 01 R90-616
		dried hops	3.15	
		spent hops	0.12	
		beer	<0.01	
		spent yeast	0.02	
Rohr[1,2]	10	fresh hops	1.12	NJ 01 R90-61B
		dried hops	3.55	
		spent hops	0.23	
		beer	<0.01	
		spent yeast	0.02	
Steinbach[1,2]	10	fresh hops	0.63	NJ 01 R90-61A
		dried hops	2.34	
		spent hops	0.14	
		beer	<0.01	
		spent yeast	0.02	
Rohr[1,2]	10	fresh hops	0.72	NJ 01 R90-61D
		dried hops	2.22	

Location, year	PHI, days	Sample	Residues, mg/kg	Ref.
		spent hops	0.12	
		beer	<0.01	
		spent yeast	0.02	

Underlined residues are from treatments according to GAP in Germany
[1] No weather data submitted
[2] Crops stored up to 13 months before analysis

Other commodites. GAP was also reported for peas in Japan and Italy and wheat in Japan, but no trials data were submitted.

Feeding trials on cattle and pigs

Twelve cattle (White Face) and twelve crossbred pigs were fed for 28 days on a diet containing nominally 0.1, 0.3 or 1.0 ppm fenarimol. The actual levels of the active ingredient in the treated feed were lower, apparently owing to the extraction procedures in which dichloromethane was used. The animals were killed 6 hours after the final feed. Tissues samples were extracted with methanol-acetonitrile, and the filtered extract partitioned with dichloromethane/aqeous NaCl. A cleaned up dichloromethane extract was then analysed by GLC with an ECD. Average procedural recoveries were 78-95% and 86-109% from cattle and pigs respectively. The residue distribution in tissues, corrected for recoveries, were as shown in Table 42 (Koons *et al*., 1984).

Table 42. Fenarimol residues in cattle and pigs.

Animal feeding level, ppm	Residue, mg/kg				
	Liver	Kidney	Muscle, loin	Muscle, round	Fat
Cattle					
0.1	0.005- 0.006	0.01	0.01	0.01	0.01
0.3	0.005-0.03	0.01	0.01	0.01	0.01
1.0	0.04-0.05	0.006-0.007	0.01	0.01	0.01
Pigs					
0.1	0.003-0.007	0.01	0.01	0.01	0.003-0.004
0.3	0.007-0.01	0.01	0.01	0.01	0.007-0.01
1.0	0.01-0.03	0.005-0.01	0.01	0.01	0.01-0.03

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were submitted.

In processing

Apples. Samples of apples with incurred residues of fenarimol were processed into juice, wet pomace following juice extraction, apple sauce, wet pomace following sauce production, and dry pomace. Samples were analysed by the method of Griggs and Decker (1981). Recoveries were variable but acceptable. Individual results are shown in Table 24 and a summary is given in Table 43.

Table 43. Summary of the distribution of fenarimol residues in apple and processed products.

Residues, mg/kg					
Whole fruit	Juice	Wet pomace from juice	Sauce	Wet pomace from sauce	Dry pomace
<0.002-0.04	<0.002-0.003	0.009-0.14	<0.002-0.009	<0.002-0.2	0.01-0.7

The residues in the wet pomace suggest that the residues were originally mainly in the peel. The individual results show that residues were generally concentrated about 2-fold from wet pomace to dry pomace during juice production, about 1-8-fold from wet pomace from sauce to dry pomace, and roughly 2-8-fold from whole fruit to wet pomace from juice (Decker and Day, 1983).

The concentration of residues between whole fruit and dry pomace is shown in detail in Table 44. Samples from the Cornel, Penn Univ and Winchester trials were soak-washed before analysis of the whole apples. The mean analytical recovery associated with the dry pomace results in these trials was high at 132%.

Table 44. Effect on residues of the production of dry pomace from whole apples.

Residues, mg/kg		Concentration factor	Ref.
Whole apple	Dry pomace		
<0.002	0.014	>7	NF 18 Cornel
0.037	0.67	18	NF 18 Penn Univ
0.017	0.20	12	NF 18 Penn Univ
0.059	0.31	5	NF 18 Winchester
0.057	0.36	6	NF 18 Winchester
0.014	0.12	9	NF 18 CMR 82-10
0.008	0.16	20	NF 18 CMR 82-10
<0.002	0.012	>6	NF 18 CMR 82-11
<0.002	0.013	>7	NF 18 CMR 82-11
0.007	0.12	17	NF 18 CMR 82-16
0.007	0.098	14	NF 18 CMR 82-16
0.004	0.068	17	NF 18 CDR 6-16
Median concentration factor		14	
Mean concentration factor		11.5	
Concentration factors excluding the trials from Cornel,		median 14	

Residues, mg/kg		Concentration factor	Ref.
Whole apple	Dry pomace		
Penn. Univ. and Winchester		mean 12.9	

Grapes. Grapes with incurred residues of fenarimol were processed into must and wine. Samples were analysed by the methods of Butcher and Perkins (1992) and Butcher (1994a). Recoveries from all substrates were acceptable. Individual results are are shown in Table 29. A summary is given in Table 45 (Butcher and Wood, 1994c).

Table 45. Distribution of fenarimol residues in grapes and processed products.

Residue, mg/kg		
Grapes	Wine	Must
0.01-0.03	<0.01	<0.01
0.02-0.04	<0.01	<0.01
0.01-0.02	<0.01	<0.01

The US residue trials on grapes included processing. Juice, pomace, raisin waste and raisins were all analysed. Most of the residue after processing was associated with the raisin waste. Further details including the individual results are shown in Table 30 (Dow Elanco Ltd., undated refs. NHO1, NHO2; Day, 1984a).

The concentration of residues from grapes to raisins is shown in Table 46 and from grapes to dry pomace in Table 47.

Table 46. Effect on residues of the production of raisins.

Residues, mg/kg		Concentration factor	Reference
Grapes	Raisins		
0.02	0.040	2.0	NH 01
0.004	0.005	1.3	NH 02
0.006	0.011	1.8	NH 02
0.004	0.004	1.0	NH 02
0.026	0.040	1.5	NH 02
0.019	0.040	2.1	NH 02
0.023	0.011	0.5	NH 17
0.024	0.015	0.6	NH 17
0.019	0.010	0.5	NH 17
0.021	0.009	0.4	NH 17
0.009	0.005	0.6	NH 17
0.046	0.017	0.4	NH 17
0.029	0.019	0.7	NH 17
0.025	0.014	0.6	NH 17
0.026	0.010	0.4	NH 17
0.029	0.012	0.4	NH 17
0.053	0.026	0.5	NH 17
0.053	0.021	0.4	NH 17
0.043	0.016	0.4	NH 17

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Residues, mg/kg		Concentration factor	Reference
Grapes	Raisins		
0.081	0.020	0.2	NH 17
0.032	0.014	0.4	NH 17
0.023	0.009	0.4	NH 17
0.024	0.007	0.3	NH 17
0.016	0.011	0.7	NH 17
0.024	0.007	0.3	NH 17
0.024	0.009	0.4	NH 17
0.024	0.020	0.8	NH 17
0.028	0.019	0.7	NH 17
0.040	0.013	0.3	NH 17
0.020	0.012	0.6	NH 17
0.009	0.012	1.3	NH 17
0.068	0.042	0.6	NH 17
0.052	0.050	1.0	NH 17
0.044	0.026	0.6	NH 17
0.040	0.023	0.6	NH 17
0.044	0.022	0.5	NH 17
0.067	0.024	0.4	NH 17
0.032	0.050	1.7	NH 17
.061	0.019	0.3	NH 17
0.061	0.015	0.2	NH 17
0.021	0.012	0.6	NH 17
0.100	0.064	0.6	NH 17
0.053	0.059	1.1	NH 17
0.085	0.034	0.4	NH 17
0.060	0.036	0.6	NH 17
0.034	0.042	1.2	NH 17
median concentration factor		0.6	

Table 47. Effect on residues of the production of dry grape pomace.

Residues, mg/kg		Concentration factor	Reference
Grapes	Dry grape pomace		
0.002	0.030	15	NH 17
0.004	0.047	12	
<0.002	0.012	>6	

In two Australian residue trials grapes were fermented into wine. The results are shown in Table 30 (NH 24). The residues in the wine were very low.

Hops. Samples of hops with incurred residues of fenarimol were processed into dried hops, beer and spent hops. Spent yeast following brewing was also analysed. Analyses were by the method of Butcher and Perkins (1992). Recoveries from all substrates were acceptable. The residues were as shown in Table 48.

Table 48. Distribution of fenarimol residues in hops and brewing products.

Residue, mg/kg				
Fresh hops	Dried hops	Spent hops	Beer	Spent yeast
0.63-1.12	2.22-3.55	0.12-0.23	0.01	0.02

Individual results (given in Table 41) showed a 3-5-fold increase in residues between fresh and dried hops and a roughly 15-25-fold decrease between dried hops and spent hops (Butcher and Perkins, 1991).

Residues in the edible portion of food commodities

Bananas. Several residue trials were carried out in which the residues in the pulp and whole bananas were determined separately. In one trial the peel was also analysed separately. Residues of fenarimol were found in the edible pulp, but were generally lower than in the peel. The results are given in Table 32 (Catta-Preta and Matos, 1993; Ishikura, 1991).

Melons. Several residue trials were carried out in which the pulp and peel were analysed separately. Residues in the pulp were low (≤0.02 mg/kg), although in most of the trials samples were taken up to 4 days after a single treatment. Details are given in Table 34.

Pecans. In thirteen US trials residues in the kernels and shells were determined separately. Residues in the edible kernels were all <0.002 mg/kg whereas residues in the shells were 0.002-0.164 mg/kg from trials at a variety of application rates. Individual results are given in Table 40 (Decker, 1983a, 1984).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Results of random monitoring analyses undertaken by the Australian Department of Primary Industries and Energy from 1st January 1989 to 30th June 1992 are shown below. Sampling of fruit and vegetables was of the whole commodity excluding stones, stems, crowns etc.

Table 49. Australian monitoring data for fenarimol.

Commodity	Residue, mg/kg	Number of samples
Apple	<0.01	45
	0.01-0.04	2
	0.05-0.1	1
	TOTAL	48
Fresh grapes	<0.01	165
	trace only	1
	0.01-0.02	10
	0.02-0.05	1

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	TOTAL	177
Pears	<0.01	17
	0.01-0.04	2
	TOTAL	19

NATIONAL MAXIMUM RESIDUE LIMITS

The national MRLs listed below were reported to the Meeting.

Country	Crop	MRL, mg/kg	Ref.
Argentina	apples	0.01	ref. 1
	grapes	0.1	
	peach	0.1	
	pear	0.01	
	squash, small	0.1	
Australia	pome fruit	0.2	ref. 2
	fruiting vegetables/cucurbits	0.2	
	grapes	0.1	
Brazil	apple	0.05	ref. 1
	cucumber	0.05	
	grapes	0.05	
	muskmelon	0.05	
	pumpkin	0.05	
	watermelon	0.05	
European Union[1]	citrus fruit	0.02*	ref. 3
	tree nuts	0.02*	
	pome fruit	0.3	
	stone fruit	(A)[2]	
	grapes, table & wine	0.3	
	strawberries	0.3	
	raspberries	0.3	
	currants	1	
	gooseberries	1	
	all other berries and small fruit	0.02*	
	root and tuber vegetables	0.02*	
	bulb vegetables	0.02*	
	fruiting vegetables	(A)	
	brassica vegetables	0.02*	
	leaf vegetables	0.02*	
	peas with & without pods	(A)	
	other legumes	0.02*	
	artichokes	(A)	
	other stem vegetables	0.02*	
	fungi	0.02*	
	pulses	0.02*	
	oil seeds	0.02*	
	potatoes	0.02*	
	tea	0.01*	
	hops	5	
	wheat/barley	(A)	
	other cereals	0.02*	

fenarimol

Country	Crop	MRL, mg/kg	Ref.
	liver/kidney	(A)	
	other meat, milk or dairy	0.02*	
Hungary	apple	0.2	ref. 1
	blueberry/gooseberry	0.2	
	cherry	0.2	
	cucurbits	0.2	
	parsley	0.2	
	vineyards	0.2	
Japan	apple	1	
	aubergine	0.5	ref. 1
	cucumber	0.5	
	melon	1	
	pea, immature	0.5	
	peach	1	
	Japanese pear	1	
	pepper, sweet	0.5	
	persimmon	1	
	pumpkin	0.5	
	strawberries	1	
	tomato	0.5	
	watermelon	1	
	wheat	0.1	
Mexico	apples	0.1	ref. 1
	grapes	0.2	
	peas	0.1	
	pecan	0.1	
USA	apple	0.1	ref. 1
	cherry	1	
	grape	0.2	
	pear	0.1	
	pecan	0.1	
	cattle, fat	0.1	
	cattle, kidney	0.1	
	cattle, liver	0.1	
	cattle, meat by-products	0.01	
	cattle, meat	0.01	
	eggs	0.01	
	goats, fat	0.1	
	goats, kidney	0.1	
	goats, liver	0.1	
	goats, meat by-products	0.01	
	goats, meat	0.01	
	hog, fat	0.1	
	hog, kidney	0.1	
	hog, liver	0.1	
	hog, meat by-products	0.01	
	hog, meat	0.01	
	horse, fat	0.1	

Country	Crop	MRL, mg/kg	Ref.
	horse, kidney	0.1	
	horse, liver	0.1	
	horse, meat by-products	0.01	
	horse, meat	0.01	
	milk	0.003	
	poultry, fat	0.01	
	poultry, meat by-products	0.01	
	poultry, meat	0.01	
	sheep, fat	0.1	
	sheep, kidney	0.1	
	sheep, liver	0.1	
	sheep, meat by-products	0.01	
	sheep, meat	0.01	

[1] Applicable to Austria, Belgium, Denmark, Germany, Greece, Finland, France, Ireland, Italy, Luxembourg, The Netherlands, Portugal, Spain, Sweden and the UK
[2] To be set at 0.02* mg/kg (analytical limit of determination) unless further residue trials data are supplied

APPRAISAL

Fenarimol is a pyrimidin-5-ylbenzhydrol systemic fungicide, which is available in several formulations, the most important being emulsifiable concentrates, suspension concentrates, and wettable powders. It is registered for use on many crops world-wide. It was considered for the first time by the present Meeting.

Fenarimol is a crystalline solid of moderately low melting point and volatility. It has low solubility in water and is soluble in medium polarity solvents. The octanol/water partition coefficient indicates that the compound has the potential to accumulate to a moderate extent. It is photolabile in air and water and is not flammable, autoflammable, explosive or oxidizing.

In rats the major metabolic routes are oxidation of the carbinol, the chlorophenyl rings and the pyrimidine ring.

In goats a number of metabolites were formed, but they occurred at very low levels and would be unlikely to exceed 0.01 mg/kg following the feeding of crops (e.g apple pomace) which had been treated according to current GAP. The metabolites included *o*-chlorobenzoic acid and the methyl sulfone derivative of fenarimol, neither of which were identified as rat metabolites. Fenarimol was also detected in liver and kidney samples at low levels, and was the major component of the residue in pigs. In a poultry metabolism study the highest total residue occurred in the liver and kidneys. No identification of the residue was attempted although intakes by chickens from treated crops are likely to low (<0.1 ppm in the diet).

In apples and grapes fenarimol was degraded to numerous unidentified compounds at very low levels. These are likely to be photo-degradation products as they generally show very similar chromatographic characteristics. They do not occur in rats. The major component of the radioactive residue in apples, grapes and cucumbers was fenarimol. Six hours, 29 days and 49 days after spraying apples with [Æ-14C]fenarimol, the majority of the radioactive residue (81-92%) was associated with the peel.

A number of analytical methods were reported for a variety of substrates. Although these used different extraction and clean-up techniques, the determination in all was by GLC with an ECD, achieving LODs of 0.002-0.05 mg/kg.

Since the studies of metabolism by plants and livestock indicated that unchanged fenarimol was the major component of the residue, the Meeting concluded that the residue should be defined as fenarimol.

Residues in wine, grapes and cherries were found to be stable for at least 370, 370 and 104 days, respectively, following storage at *c.* -20°C. Additional data on the storage stability of residues were available for fortified peaches, tomatoes and melons, but were submitted too late for consideration by the Meeting: they will be evaluated by a future Meeting.

Important experimental details were missing from several of the residue trials. In cases where weather data, example chromatograms, crop variety or full details of the method of analysis for the particular trial were not provided the trials data were used, where applicable, to estimate maximum residue levels, since these omissions were not considered critical. However, where analytical recoveries associated with a trial were outside the range 70-120% the results were generally ignored. Similarly, if laboratory samples were stored frozen for more than 6 months or the duration and conditions of storage were unspecified the analytical results were not considered reliable. The exception to this was fruit crops for which data on the storage stability of residues were available. Finally in all cases a study report was considered necessary; a simple trial sheet was not considered to give sufficient information and such submissions as were not used in the estimation of maximum residue levels.

Apples. The results of a large number of trials were available from several countries around the world. The highest residues were found in trials according to Dutch GAP, but since the Dutch data were submitted only in summary form they were not used to estimate maximum residue levels. 16 Northern European trials reflected German GAP (0.0036 kg ai/hl, 21-day PHI) with residues of 0.02-0.21 mg/kg. A number of other German trials were reported but only summary sheets were submitted. US GAP was followed in eight trials in the USA, several of which were replicated, with residues 29-42 days after the final treatment of 0.002-0.059 mg/kg.

Eight trials according to GAP reported for Denmark, the UK and Ireland showed residues of 0.02-0.18 mg/kg. In further trials according to GAP in New Zealand, Brazil and Chile residues were 0.002-0.09 mg/kg. The Meeting estimated a maximum residue level of 0.3 mg/kg.

Pears. Four trials according to GAP were reported from the USA with residues of 0.01-0.04 mg/kg. Two trials were available with residues up to 0.13 mg/kg reflecting Italian and German GAP: the analytical recoveries associated with these trials were low at 63 and 67% respectively. The Meeting took into account the large number of trials on apples and the similar use patterns on the two crops, and estimated a maximum residue level of 0.3 mg/kg for pome fruits.

Peaches. Five peach trials in Spain and Italy according to Spanish GAP gave residues of 0.03-0.3 mg/kg at 7 days. In two of these trials the volume of spray per hectare was not clear and the results can therefore only be used as supplementary information. A further 1988 Spanish trial on apricots according to Spanish GAP for peaches with a residue of 0.36 mg/kg at 7 days provides support. The highest residues were from trials in which high water volumes were used but these complied with GAP. In a single Chilean nectarine trial according to Argentinian GAP residues were below the LOD at 2 days. No trials were available with results at the Japanese GAP PHI of one day. The Meeting estimated a maximum residue level of 0.5 mg/kg for peaches.

Cherries. Nine trials (3 with replicates) according to US GAP showed residues of 0.06-0.89 mg/kg at a 0- or 1-day PHI. It was recognised that no account was taken of the weights of the stones and the residues in the whole cherries would have been somewhat lower. The Meeting estimated a maximum residue level of 1 mg/kg for cherries.

Currants. Only 5 trials were available from The Netherlands and only one of these was according to GAP in Denmark, Ireland, The Netherlands or the UK. Furthermore, since the Dutch data were submitted only in summary form they could not be used. The Meeting concluded that there were insufficient data to estimate a maximum residue level for currants.

Gooseberries. Only one Dutch trial, reported in summary form only, was available: it complied with GAP reported for Ireland, The Netherlands and the UK. The Meeting concluded that there were insufficient data to estimate a maximum residue level.

Grapes. Residues in grapes treated according to GAP in the USA, Australia and France were generally low with residues of 0.003-0.06 mg/kg, 0.01-0.08 mg/kg and 0.02 mg/kg, respectively. A number of German trials were submitted of which six (2 with replicates) reflected German GAP (0.023 kg ai/ha, 35-day PHI). The residues were 0.01-0.15 mg/kg in samples taken 35 days after the final treatment. Seven of the German trials (two with replicates) which accorded with UK GAP (0.04 kg ai/ha, PHI 14 days) gave residues of 0.02-0.24 mg/kg in samples taken 14 days after the final treatment. There were no southern European trials at the highest GAP rate (0.06 kg ai/ha) or the shortest PHI (7 days). The Meeting estimated a maximum residue level of 0.3 mg/kg for grapes.

Strawberries. Residue trials data were available from Italy, Japan, Spain and The Netherlands. Three Italian trials were according to GAP (0.048 kg ai/hl, 7-day PHI), with residues of 0.12-0.18 mg/kg. Dutch trials reflecting GAP (0.084 kg ai/ha, treatment before flowering) showed residues of <0.01-0.02 mg/kg, but the data were submitted in summary form only and were therefore not considered further. Higher residues would result from Spanish GAP which has the shorter PHI of 3 days (0.0048 kg ai/hl) and which was represented by one trial with a residue of 0.25 mg/kg. Seven field trials were according to Japanese indoor GAP with a PHI of 1 day (0.03 kg ai/ha or 0.003 kg ai/hl). Residues in crops sampled one day after the final treatment were 0.04-0.56 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for strawberries.

Raspberries. Only one residues trial was available from the UK and this was at a higher application rate than the GAP reported for Ireland and the UK. There were insufficient data to estimate a maximum residue level.

Bananas. Residue trials in Ecuador, Costa Rica and Honduras demonstrated that residues in unbagged bananas were generally higher than in bagged bananas. Six trials according to GAP in Honduras and Nicaragua (0.12 kg ai/ha, PHI 0 days) showed residues in unbagged bananas 0 or 1 day after the final treatment of <0.01-0.19 mg/kg. Six further trials at twice the registered application rate led to residues of 0.03-0.3 mg/kg in unbagged fruit. Residues were determined in the edible pulp. Although these were generally lower than those in the peel some were higher. The Meeting concluded that there was no consistent partition factor between the pulp and peel. It estimated a maximum residue level of 0.2 mg/kg.

Cucumbers. Only very limited data were available with one trial according to UK and Irish GAP (0.002 kg ai/hl, 2-day PHI) and one according to GAP in Uruguay. Residues were 0.03 mg/kg after 2 days and 0.003 mg/kg after 4 days respectively. The Meeting concluded that there were insufficient data to estimate a maximum residue level for cucumber.

Gherkins. Information on GAP gherkins in The Netherlands was reported as 0.0024 kg ai/hl, 6-day PHI, for both protected and field use. Two Dutch trials were reported with the high application concentration of 0.24 kg ai/hl but with the rate per hectare unspecified. However, since the data were submitted in summary form only they were unsuitable. The Meeting concluded that there were insufficient data to estimate a maximum residue level.

Melons (including cantaloupe) and watermelons. Data were available from two Spanish indoor trials but these were with a higher spray concentration than the reported Dutch GAP. Two trials were according to Brazilian GAP (0.024 kg ai/ha, 4-day PHI); the residues were 0.005 mg/kg in melons and "not detected" in watermelons.

Four French trials on melons were according to Greek GAP for "cucurbits" (0.024 kg ai/ha, 1-day PHI) with residues of <0.01 mg/kg in the pulp and up to 0.11 mg/kg in the peel of samples taken 2 days after the final treatment. However, no information was available on the weight ratio of the peel to the pulp. The manufacturer suggested a 30% peel to fruit weight ratio based on melon samples taken from other trials. Whilst the Meeting would not normally consider it appropriate to use an assumed weight ratio, this was considered an exceptional case since the residues were very low and calculations of the residues in whole melons from the trial with the highest residue level in the peel, based on an assumed peel:fruit weight ratio of 20-40%, would lead to values of 0.03-0.05 mg/kg if the residues in the pulp were at the limit of determination. Other trials were available which, although they did not correspond exactly to reported GAP (usually they were with exaggerated doses), indicated that residues were generally low. The Meeting estimated a maximum residue level of 0.05 mg/kg for melons. Since there were relatively few results the Meeting did not consider it appropriate to extrapolate this estimate to other cucurbits.

Pumpkins, courgettes and squashes. Only limited data were available, with no indoor trials according to Dutch indoor GAP.

Only one trial in Brazil, with a residue of 0.005 mg/kg, conformed to outdoor GAP in Argentina and Uruguay. Single Australian replicated trials on zucchini and pumpkins were according to Australian GAP for cucurbits. Residues were very low: 0.001-0.01 mg/kg three days after the final treatment. The Meeting concluded that there were insufficient data to estimate a maximum residue level for pumpkins, courgettes or squashes.

Tomatoes. Two indoor trials in The Netherlands were comparable to Danish GAP (0.036 kg ai/ha or 0.0048 kg ai/hl, 2-day PHI). Residues in both were 0.03 mg/kg at 2 days. Italian and Spanish outdoor GAP (0.0048 and 0.006 kg ai/hl, 7-day PHI) was reflected in two Italian trials and one Spanish trial with residues of 0.03, 0.03 and 0.05 mg/kg at 7 days. There were no outdoor trials according to Japanese GAP, which has a PHI of 1 day. Should submissions be made in the future, processing data will be required. There were insufficient data to estimate a maximum residue level.

Peppers. There were 6 trials in Italy and Spain according to Italian and Spanish GAP (the same as for tomatoes). The residues were 0.03 and 0.07 mg/kg in the Italian trials and 0.07, 0.08, 0.12 and 0.5 mg/kg in the Spanish trials, in samples taken 7 days after the final treatment. The Meeting estimated a maximum residue level of 0.5 mg/kg for peppers.

Aubergines. Only one Italian trial was available in which the residue was <0.01 mg/kg 15 days after treatment. This was insufficient to estimate a maximum residue level.

Beetroots and carrots. The only GAP reported for beetroots and carrots was the Dutch GAP for "vegetables" (0.036 kg ai/ha or 0.0024 kg ai/hl, 3-day PHI). Although one Netherlands trial was available for each of these crops, neither reflected GAP since samples were taken 27 days after treatment. No maximum residue level could be estimated.

Artichoke, Globe. Six Italian trials were considered to reflect Italian GAP (0.0048 kg ai/hl or 0.038 kg ai/ha, 7-day PHI) with residues of <0.01-0.06 mg/kg. Two of these trials (in 1979 with residues of <0.01 and 0.03 mg/kg) had a low associated analytical recovery (61%) and were therefore not considered reliable. A further Spanish trial gave a higher residue of 0.26 mg/kg at 7 days but a high volume of water (2,500 l/ha) was applied and the spray concentration (0.006 kg ai/hl) was higher than that registered in Italy. The Meeting estimated a maximum residue level of 0.1 mg/kg for globe artichokes.

Witloof chicory. Only one replicated trial in The Netherlands was available which complied with Dutch GAP for "vegetables". Residues were <0.01 mg/kg in samples taken 60 days after treatment. The Meeting concluded that there were insufficient data to estimate a maximum residue level for witloof chicory.

Pecans. Twelve trials were carried out in the USA of which four (one replicated) had application rates of 0.074-0.12 kg ai/ha, close to the registered rate in the USA (0.098 kg ai/ha). Residues in the kernels, to which the MRL applies, were <0.002 mg/kg at 35-153 days. In a further series of trials, residues in the kernels were all <0.002 mg/kg except in one trial with 0.02 mg/kg, at an exaggerated application rate (0.14-0.197 kg ai/ha). The residue of 0.02 mg/kg may have resulted from physical transfer from the shell. Recognising the need to establish MRLs at levels suitable for routine analysis by monitoring and enforcement laboratories, the Meeting estimated a maximum residue level of 0.02* mg/kg for pecans.

Hops. Four trials in Germany were all according to German GAP (0.06 kg ai/ha or 0.0015 kg ai/hl, 10-day PHI). The residues in dry hops harvested 10 days after the final treatment were 2.22-3.55 mg/kg, but in all the trials the hop samples were stored for 13 months before analysis. Brewing with these hops gave residues in the beer of <0.01 mg/kg. The results appeared very consistent and would suggest a maximum residue level of 5 mg/kg in dry hops, but in the absence of data confirming the stability of fenarimol in stored samples of a leafy crop the Meeting decided not to recommend an MRL: it was informed that a storage stability study on hops was now available.

Apple pomace. Processing data on apples indicated a concentration of residues from whole apples to dry pomace of 5-20-fold, with a median concentration factor of 14. Apple samples in several of the trials were "soak-washed" before analysis of the whole apples. The Meeting considered the data from these samples unsatisfactory. In the seven remaining trials with unwashed apples the median and mean concentration factors were 15 and 17 respectively. Although it was noted that the analytical recoveries from dry apple pomace were variable (68, 68, 76, 83, 108, 132 and 132%) the Meeting estimated a maximum residue level of 5 mg/kg for apple pomace, dry.

Dried grapes. Processing data on grapes indicated concentration factors for residues in whole grapes to those in raisins of 0.2-2.1. By applying the median concentration factor of 0.6 to the estimated maximum residue level of 0.3 mg/kg for grapes, the Meeting estimated a maximum residue level of 0.2 mg/kg for dried grapes.

Grape pomace, dry. Processing grapes to dry grape pomace increased the residues about 12-15 times, but as there were only two suitable results and residues in the grapes were low the Meeting could not establish a reliable concentration factor and therefore did not estimate a maximum residue level.

In a livestock feeding study beef cattle and pigs were fed for 28 days with fenarimol at various rates up to 1 ppm in the diet. At this dose residues of fenarimol in all tissue except liver were ≤0.01 mg/kg. Residues in the liver reached a maximum level of 0.03 mg/kg in pigs and 0.05 mg/kg in cattle. At rates of 0.1 and 0.3 ppm all tissue residues were <0.01 mg/kg.

Livestock will obtain fenarimol from wheat grain and straw, peas and pea straw, and fruit pomace. Of these items sufficient data on residues were available only for dry apple pomace (estimated maximum residue level 5 mg/kg). Dairy and beef cattle consume a maximum of 30% of their dietary dry matter as fruit pomace, whereas it is not generally fed to pigs. The maximum intake of fenarimol by beef cattle from fruit pomace would therefore be approximately 1 ppm in the diet. The Meeting recognized the need to establish MRLs at levels suitable for routine analysis by monitoring and enforcement laboratories, and estimated maximum residue levels of 0.02* mg/kg for cattle meat and kidney and 0.05 mg/kg for cattle liver.

There were insufficient data on pig feed items to estimate a maximum residue level for the meat or edible offal of pigs.

Although data on the environmental fate of fenarimol in soil were submitted to the Environmental Core Assessment Group at the present Meeting they were not, as would normally be expected, submitted for the consideration of the FAO Panel. The manufacturer agreed to submit the data to the FAO, for future consideration by the FAO Panel, as soon as possible. The Meeting concluded that in these circumstances temporary MRLs should be recommended, with a requirement for the studies on environmental fate.

RECOMMENDATIONS

The Meeting estimated the temporary maximum residue levels shown below, which are recommended for use as TMRLs.

Definition of the residue: fenarimol

CNN	Commodity	Recommended MRL, mg/kg	PHI on which based, days
AB 0266	Apple pomace, dry	5T	-
VS 620	Artichoke, Globe	0.1T	7
FI 327	Banana	0.2T	0
MM 812	Cattle meat	0.02*T	-
MO 1280	Cattle kidney	0.02*T	-
MO 1281	Cattle liver	0.05T	-
FS 13	Cherry	1T	0
DF 269	Dried grape	0.1T	-
FB 269	Grape	0.3T	14
VC 46	Melons, except Watermelon	0.05T	1
FS 247	Peach	0.5T	7
TN 672	Pecan	0.02*T	30
VO 445	Peppers, Sweet	0.5T	7
FP 9	Pome fruits	0.3T	14-28
FB 275	Strawberry	1T	1

FURTHER WORK OR INFORMATION

Required (by 1996)

Data on the environmental fate of fenarimol in soil.

Desirable

1. Full details of the methods of analysis used in all the residue studies where this information was not given. Validation of the methods of analysis for which validation data were not submitted.

2. A study to assess the likely residues in relevant succeeding or rotational crops or an explanation of why residues would not be expected.

3. Information on the melting point, octanol/water partition coefficient, solubility and specific gravity of pure fenarimol.

4. Submission of the study reports supporting the trials on apples, gooseberries, currants, gherkins and strawberries conducted in The Netherlands.

fenarimol

REFERENCES

Althaus, W.A. 1982a. ^{14}C Fenarimol Chicken Tissue Residue Study. Sept ABC-0186. Ref. NA 06.

Althaus, W.A. 1982b. ^{14}C Fenarimol Chicken Egg Residue Study. Sept ABC-0147. Ref. NA 07.

Althaus, W.A. 1984a. A Comparative Apple Residue Study Conducted with Carbinol-labelled and mixed-labelled ^{14}C Fenarimol. Mar ABC-0199. Ref. L 02.

Althaus, W.A. 1984b. ^{14}C Fenarimol Grape Residue Study. Apr ABC-0237, ABC-0239. Ref. L 03.

Althaus, W.A. 1985a. Characterization and Identification of Radioactivity in Urine and Feces of Wistar Rates given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0310. Ref. H 10.

Althaus, W.A. 1985b. Characterization and Identification of Radioactivity in Blood, Liver, and Kidney of Wistar Rats given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0321. Ref. H 11.

Althaus, W.A. 1986. ^{14}C Fenarimol Residue Study in Cucumbers. Oct ABC-0307. Ref. L 08.

Althaus, W.A. and Bewley, G.W. 1978a. ^{14}C Fenarimol Apple Residue Study Jan Ref. L 09.

Althaus, W.A. and Bewley, G.W. 1978b. Separation and Identification of Degradation Products formed from ^{14}C Fenarimol Applied to Apples. Jan Ref. L 01.

Althaus, W.A. *et al.* 1984. ^{14}C Fenarimol Swine Tissue Residue Study. Apr ABC-0202. Ref. NA 09.

Arcas, J.B. 1986. Analises de Residuos de Fenarimol em Frutos e Cucurbitaceas Ref. NB 29.

Arnold, M. 1995. Dow Elanco Europe. Spanish residue trials data for apricots, peaches, melons, artichoke, peppers and strawberry submitted with letter dated 17th July Unpublished. Ref. 13.

Arnold, M. 1995. Dow Elanco Europe. Personal Communication. 16th August Ref. 10.

Butcher, S.M. 1992. Determination of Fenarimol Residues in Beer and Spent Yeast. Jan ERC91-10. Ref. OR 21.

Butcher, S.M. 1993. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12ec (EAF 457), Spain Aug 1994 GHE-P-3653. Ref. NE 08.

Butcher, S.M. 1994a. Determination of Residues of Fenarimol in Tomatoes, Peaches and Melons ERC 94.3 Aug Ref. OR 24.

Butcher, S.M. 1994b. The Stability of Fenarimol in Fortified Grapes and Wine stored under Frozen Conditions GHE-P-3741 Aug Ref. NH 10.

Butcher, S.M. 1995a. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12SC (EAF 383), Netherlands Jan 1995. GHE-P-4008. Ref. NE 11.

Butcher, S.M. 1995b. Residues in Melons Spain Jan 1995 GHE-P-4011. Ref. NB 31.

Butcher, S.M. 1995c. Residues of Fenarimol in Tomatoes - Greece Jan 1995. GHE-P-4012. Ref. NE 12.

Butcher, S.M. 1995d. Residues in Melons Italy Jan 1995 GHE-P-4013. Ref. NB 32.

Butcher, S.M. 1995e. Peaches Italy Jan GHE-P-4014. Ref. NG 10.

Butcher, S.M. 1995f. Peaches France Jan GHE-P-4062. Ref. NG 11.

Butcher, S.M. 1995g. The stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditons. GHE-P-4318. Ref. NG 12.

Butcher, S.M. 1995h. Residues of Fenarimol in Globe Artichokes at Intervals following Multiple Applications of RUBIGAN 12 SC (EAF383), Italy GHE-P4010 Jan 1995. Ref. NI 05.

Butcher, S.M. and Long, T.J. 1993. Determination of Residues of Fenarimol in Grape Must, Wine and Grapes. ERC93-6 Jul Ref. OR 22.

Butcher, S.M. and Perkins, J. 1991. Residues of fenarimol in Hops and related fractions from the brewing process following application of Drawisan 6WP (EAF 219) - Germany 1990. GHE-P-2517 Oct Ref. NJ 01.

Butcher, S.M. and Perkins, J.M. 1992. Determination of Fenarimol Residues in Fresh, Dried and Spent Hops. ERC91-8 Jan Ref. OR 20.

Butcher, S.M. and Wood, S. 1994a. Residues of Fenarimol in Grapes at Intervals following Application of TRANSFLO (EAF 383), France - GHE-P-3627 Jun 1994. Ref. NH 04.

Butcher, S.M. and Wood, S. 1994b. Residues of Fenarimol in Peaches at intervals following Application of RUBIGAN 12sc (EAF383), Italy - GHE-P-3626 Jun 1994. Ref. NG 08.

Butcher, S.M. and Wood, S. 1994c. Residues of Fenarimol in Grapes, Grape Must and Wine following Application of Rubigan 12 SC (EAF 383) to Grape Vines Germany GHE-P-3655 Aug 1994. Ref. NH 11.

Butcher, S.M. and Wood, S. 1994d. Residues of Fenarimol in Peaches at intevals following Application of RUBIGAN 4 (EAF 216), - Southern France GHE-P-3652 Aug 1994. Ref. NG 07.

Catta-Preta, R.F. and Matos, J.C. 1992 Residues of Fenarimol and its Major Metabolites in Bananas following Multiple treatments with Rubigan Ec Fungicide - Costa Rica, Honduras and Ecuador, April 1993 GHB-P 151. Ref. NL 02.

Catta-Preta, R.F. and Matos, J.C. 1993. Determination of

Residues of Fenarimol, Compound 212746 and 210302 in Banana Whole Fruit and Pulp BRC 92.2 March Ref. R 28.

Coleman, I. 1995. Commonwealth Department of Primary Industries and Energy, Australia. Personal Communication. 12th April Ref. 2.

Cowlyn, T.C. 1992. Fenarimol (pure): Determination of Physico-Chemical Properties (Vapour Pressure) Sept 93/DES080/0411. Ref. A 21.

Cowlyn, T.C. 1992. Fenarimol (technical): Determination of Physico-Chemical Properties (Flammability, Auto-flammability, Explosive and Oxidising Properties) Oct 92/DES081/0866. Ref. A 22.

Crossley, S.J. 1994. Pesticides Safety Directorate, UK. Personal Communication. 31st November Ref. 9.

Day, E.W. 1976. Solubility of Fenarimol in Organic Solvents. Sept FLP V-131. Ref. A 09.
Day, E.W. 1981. Fenarimol Residue Data on Apples from Canada May Ref. NF 27.

Day, E.W. 1981. Fenarimol Residues in Apples from New Zealand Mar NZ75-19, 1988 NZ78-2, NZ80-5, NZ80-6. Ref. NF 29.

Day, E.W. 1981. Fenarimol Residues in Apples from Chile May T2R-230. Ref. NF 28.

Day, E.W. 1983. Fenarimol Residue Data on Grapes and Grape Products from Experiment conducted in the United States in March 1984 I-EWD-84-03. Ref. NH 17.

Day, E.W. 1985. Fenarimol Technical Product Chemistry Data. Ref. A 08.

Day, E.W. 1987. Fenarimol Residue Data on Pears March EWD8640. Ref. NF 33.

Day, E.W. 1993. Reasonable Grounds in Support of the Petition for the Establishment of A Tolerance for Fenarimol and its Metabolites in or on Bananas. Aug ECL93073. Ref. NL

Day, E.W. Undated. Preliminary Photochemical Studies with the Fungicide EL-222. Ref. K 26.

Day, E.W and Saunders, D.G. 1987. Fenarimol Residue Studies in Cherries AAC8713 Feb 1988. Ref. NG 04.

Day, E.W. and Saunders, D.G. 1988. Storage Stability of Fenarimol in Cherries EWD8803 Feb Ref. NG 06.

Day, E.W. Jr. and Saunders D.G. 1988. Storage Stability of Fenarimol and its Metabolites in Grapes and Grape Products. EWD8802 Apr Ref. NH 07.

Day, E.W. and West, S.D. 1988. Fenarimol Residue Studies in Apples Nov 1988. AAC8819. Ref. NF 31.

Day, E.W. and West, S.D. 1988 Fenarimol Residue Trials in Grapes AAC8818 Dec 1988. Ref. NH 20.

Day, E.W. and West, S.D. 1989. Fenarimol Residue Studies in Cherries, Aug 1989 AAC8903. Ref. NG 05.

Day, E.W. *et al.* 1984. Physical and Chemical Characteristics of Technical Fenarimol Nov EWD8450. Ref. A 14.

Decker, O.D. 1983. Fenarimol Residues on Pecans when Rubigan 1EC or Rubigan 1AS is Foliar applied to Pecan Trees on Disease Control March I-ODD-82-02. Ref. NM 01.

Decker, O.D. 1984. Fenarimol Residues on Pecans when Rubigan is Foliar applied to Pecan Trees for Disease Control Feb I-ODD-84-01. Ref. NM 02.

Decker, O.D. and Day, E.W. 1981. Fenarimol Residue Data on Apples and Apple Products from Experiments conducted in the United States in and 1982. Mar 1983. I-ODD-83-06. Ref. NF 18.

Dow Elanco Ltd. 1976. Determination of EL-222 in Agricultural Crops and Soils by Gas-Liquid Chromatography Std An.Method No.86 Sep Ref. OR 10.

Dow Elanco Ltd. 1976. Residue Study - Cucumber - Austria A76-106. Ref. NB 01.

Dow Elanco Ltd. 1976. Residue Study - Melon- France F76-04. Ref. NB 02.

Dow Elanco Ltd. 1976. Residue Study-Cucumber-Italy 176-33. Ref. NB 03.

Dow Elanco Ltd. 1976. Residue Study - Cucumber - UK FG76-016. Ref. NB 04.

Dow Elanco Ltd. 1977. Determination of Fenarimol In Agricultural Crops (Other than Cereals) by Gas-Liquid Chromatography Nov Std.An.Method No.97. Ref. OR 11.

Dow Elanco Ltd. 1977. Residue Study - Cucumber - Italy 177-234. Ref. NB 08.

Dow Elanco Ltd. 1977. Residue Study - Cucumber - Italy 177-235. Ref. NB 09.

Dow Elanco Ltd. 1977. Residue Study - Squash - Italy 177-236. Ref. NB 10.

Dow Elanco Ltd. 1977. Residue Study - Cantaloupe - Italy 177-251. Ref. NB 11.

Dow Elanco Ltd. 1977. Residue Study - Watermelon - Italy 177-253. Ref. NB 12.

Dow Elanco Ltd. 1977. Residue Study - Peppers - Spain E77-129. Ref. NE 02.

Dow Elanco Ltd. 1977. Residue Study - Peach - Italy 177-212. Ref. NG 01.

Dow Elanco Ltd. 1977. Residue Study - Peach 177-213. Ref. NG 02.

Dow Elanco Ltd. 1977. Residue Study - Peach - Italy 177-214. Ref. NG 03.

Dow Elanco Ltd. 1977. Residue Study - Grape A77-121. Ref. NH 05.

Dow Elanco Ltd. 1977. Residue Study - Grape A77-122. Ref. NH 06.

Dow Elanco Ltd. 1977. Residue Study - Grape 177-225. Ref. NH 09.

Dow Elanco Ltd. 1978. Residue Study - Pears - Germany D78-312. Ref. NF 03.

Dow Elanco Ltd. 1978. Residue Study - Apples - Germany D78-311. Ref. NF 08.

Dow Elanco Ltd. 1979. Residue Study - Artichoke - Italy 179-251. Ref. N1 02.

Dow Elanco Ltd. 1979. Residue Study - Strawberry - Italy 179-252. Ref. NC 11.

Dow Elanco Ltd. 1979. Residue Study - Strawberry - Italy 179-253. Ref. NC 12.

Dow Elanco Ltd. 1979. Residue Study - Tomatoes - Italy 179-251. Ref. NE 03.

Dow Elanco Ltd. 1979. Residue Study - Peppers - Israel ISL79-2. Ref. NE 04.

Dow Elanco Ltd. 1979 Residue Study - Pepper - Italy 179-250. Ref. NE 05.

Dow Elanco Ltd. 1979 Residue Study - Pepper - Italy 179-251. Ref. NE 06.

Dow Elanco Ltd. 1979. Residue Study - Tomatoes - Italy 179-250. Ref. NE 07.

Dow Elanco Ltd. 1979. Residue Study - Artichoke - Italy 179-250. Ref. NI 01.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-729. Ref. NB 20.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-730. Ref. NB 21.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-730A. Ref. NB 22.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-735. Ref. NB 23.

Dow Elanco Ltd. 1981/2. Residues Studies - Grapes - Germany and France Apr 1983. Ref. NH 12.

Dow Elanco Ltd. 1981. Residue Studies-Apples Germany and UK/Apr 1983. D81-302, D81-350, D81-351, D81-353, FF81-002. Ref. NF 20.

Dow Elanco Ltd. 1981. Residue Study - Cucumbers - Italy 181-255. Ref. NB 15.

Dow Elanco Ltd. 1981. Residue Study - Cantaloup - Italy 181-256. Ref. NB 24.

Dow Elanco Ltd. 1981. Residue Study - Squash - Italy 181-254. Ref. NB 26.

Dow Elanco Ltd. 1981. Residue Study - Artichokes - Italy 181-251. Ref. NB 28.

Dow Elanco Ltd. 1981. Residue Study - Tomatoes - Italy 181-258. Ref. NE 09.

Dow Elanco Ltd. 1981. Residue Study - Pepper - Italy 181-259. Ref. NE 10.

Dow Elanco Ltd. 1981. Residue Study - Pears - Italy 181-211. Ref. NF 06.

Dow Elanco Ltd. 1982. Residue Studies - Apples Germany Apr 1983. D82-301, D82-302, D82-303, D82-304, D82-305, D82-307. Ref. NF 21.

Dow Elanco Ltd. 1987. Submission to T.C.A.C - Rubigan Data Supporting Reduction in Withholding Period in Grapes (contains Australian Residue data) July Ref. NH 23.

Dow Elanco Ltd. 1993. Residues in Nectarines in Chile, Gonzalez, R.H Degradacion de Residous de Rubigan en Nectarinos Y Fijacion de Carencias Preliminares Chile Ref. NG 09.

Dow Elanco Ltd. 1994. Europe. Italian GAP for peaches. 17th July Unpublished. Ref. 12.

Dow Elanco Ltd. 1995. Summary of Data, Fenarimol JMPR, March Unpublished. Ref. 1.

Dow Elanco Ltd. 1995. Product Labels, Fenarimol JMPR, March Unpublished. Ref. 4.

Dow Elanco Ltd. 1995. Residues of fenarimol in fresh and processed grapes after treating Cabernet Sauvignon and Sultana grapevines with Rubigan 120 EC®. March. Ref. NH 24.

Dow Elanco Ltd. Undated. Residue Study - Grapes AAC8714. Ref. NH 01.

Dow Elanco Ltd. Undated. Residues Study - Grapes EWD8703. Ref. NH 02.

Dow Elanco Ltd. Undated. Application for clearance of RUBIGAN systemic Fungicide to the Technical Committee on Agricultural Chemicals Section E-Residues (Australian Data Summary). Ref. NB 30.

Dow Elanco Ltd. Undated. Rate of Hydrolysis of EL-222. Ref. K 25.

European Union. 1994. Council Directives 94/29/EEC and 94/30/EEC. July Ref. 3.

Frank, R. 1977. Fenarimol Residues in Whole Apple Fruit

(Canada) May T2R-233. Ref. NF 25.

Frank, R. 1978. Fenarimol Residues in Whole Apple Fruit (Canada) July T2R-198. Ref. NF 26.

Germany. 1994. Submission made by the Federal Biological Research Centre for Agriculture and Forestry, July 1994. Unpublished. Ref. 8.

Goebel, G.V. 1985a. Characterization of Radioacativity in bile from rats dosed orally with ^{14}C Fenarimol. May ABC-0312. Ref. H 04.

Goebel, G.V. 1985b. Isolation and Identification of "Metabolite Complex" from 14C Fenarimol-Treated Grapes Mar ABC-0316. Ref. L 04.

Griggs, R.D and Decker, O.D. 1981. Determination of Fenarimol in Agricultural Crops and Soil Jan AM-AACA-R039-AA-755. Ref. OR 01A.

Griggs, R.D. and Decker, O.D. 1985. Determination of Fenarimol in Agricultural Crops and Soil Jan AM-AA-CA-RO39-AB-755. Ref. OR 01B.

Hudson, J.L. 1987. Fenarimol Technical, Bulk Density, Part 158 Product Chemistry Requirement. Nov T2R908703. Ref. A 10.

Ishikura, H. 1991. Residues of Fenarimol in Pulp, Peel and Whole Bananas Following application of Rubigan 12EC Fungicide in the Philippines - July 1991. GHF-P -1126. Ref. NL 03.

Koons, J.R. *et al*. 1984. Determination of Tissue Residues in Swine and Beef Cattle Fed Diets Containing Fenarimol. Mar S-AAC-83-04. Ref. NA 10.

Loh, A. 1976. n-Octanol-To-Water Partition Coefficient of Fenarimol. Dec EWD 8742. Ref. A 17.
Longhurst, C. 1985. Residues of Fenarimol in Raspberries following Foliar Applications of RUBIGAN Sept FF84-006. Ref. ND 01.

Lunn, D.W. 1995. Ministry of Agriculture and Fisheries, New Zealand. Personal Communication. 25th May Ref. 5.

Mason, R. 1995. Pesticides Safety Division, MAFF, UK. Personal Communication. 9th September Ref. 11.

McCorquodale, G.Y. and Prout, M.S. 1994. The disposition of [^{14}C]-fenarimol in the lactating goat. DowElanco Ltd., Report No. 10422. Ref. H 17.

Mosier, J.W. and Saunders, D.G. 1976. Photochemical Studies with Fenarimol. Aug Ref. K 28.

Netherlands, Ministry of Welfare, Health and Cultural Affairs, 1994. Netherlands. Personal Communication. September 1994. Ref. 6.

Pastor Talledo, C. 1994. Direccion de hygiene, Alimentarius y Control de Zoonosis, Peru. Personal communication. 23th November Ref. 7.

Rainey, D.P. 1987. Supplementary Information on Metabolism of ^{14}C Fenarimol in Grapes. Nov ABC-0239S. Ref. L 05.

Dow Elanco Ltd. 1988. Rubigan 12 WP/Strawberry Crop Residue Study: Japan 1984 and 1988 Studies 1994. June 1988 T2R-077. Ref. NC 16.

Trevallyn-Jones, J. 1984. Further Submission to T.C.A.C. - Withholding Period in Grapes treated with RUBIGAN (contains Australian Dow Elanco Ltd. Residue data) July Ref. NH 22.

Turner, L.G. 1992. [where has the DL come from?] Dow Elanco 1982. Ltd. Residue Method Development Report for Fenarimol and its Metabolites in Whole Bananas and Banana Pulp. GH-C-2840 Aug

Yordy, D.W. and Turner, L.G. Determination of Fenarimol In Meat, Milk and Eggs. AM-AA-CA-RO72-AA-755 Sep Ref. OR 27. Ref. OR 19.

NUMERICAL REFERENCES

1. Dow Elanco Ltd. Summary of Data, Fenarimol JMPR, March 1995. Unpublished.

2. Coleman, I. Commonwealth Department of Primary Industries and Energy, Australia. Personal Communication. 12th April 1995.

3. European Union Council Directives 94/29/EEC and 94/30/EEC. July 1994.

4. Dow Elanco Ltd. Product Labels, Fenarimol JMPR, March 1995. Unpublished.

5. Lunn, D.W. Ministry of Agriculture and Fisheries, New Zealand. Personal Communication. 25th May 1995.

6. Netherlands, 1994. Ministry of Welfare, Health and Cultural Affairs, Netherlands. Personal Communication. September 1994.

7. Pastor Talledo, C. 1994. Direccion de hygiene, Alimentarius y Control de Zoonosis, Peru. Personal communication. 23th November 1994.

8. Germany, 1994. Submission made by the Federal Biological Research Centre for Agriculture and Forestry, July 1994. Unpublished.

9. Crossley, S.J. Pesticides Safety Directorate, UK. Personal Communication. 31st November 1994.

10. Arnold, M. Dow Elanco Europe. Personal Communication. 16th August 1995.

11. Mason. R. Pesticides Safety Division, MAFF, UK. Personal Communication. 9th September 1995.

12. Dow Elanco Europe. Italian GAP for peaches. 17th July 1994. Unpublished.

13. Arnold, M. Dow Elanco Europe. Spanish residue trials data for apricots, peaches, melons, artichoke, peppers and strawberry submitted with letter dated 17th July 1995. Unpublished.

A 03. Decker, O.D. Solubility of Fenarimol in Water Oct 1987 ODD8711.

A 08. Day, E.W. Fenarimol Technical Product Chemistry Data. 1985.

A 09. Day, E.W. Solubility of Fenarimol in Organic Solvents. Sept 1976 FLP V-131.

A 10. Hudson, J.L. Fenarimol Technical, Bulk Density, Part 158 Product Chemistry Requirement. Nov 1987 T2R908703.

A 14. Day, E.W. *et al*. Physical and Chemical Characteristics of Technical Fenarimol Nov 1984 EWD8450.

A 17. Loh, A. n-Octanol-To-Water Partition Coefficient of Fenarimol. Dec 1976. EWD 8742.

A 21. Cowlyn, T.C. Fenarimol (pure): Determination of Physico-Chemical Properties (Vapour Pressure) Sept 1992 93/DES080/0411.

A 22. Cowlyn, T.C. Fenarimol (technical): Determination of Physico-Chemical Properties (Flammability, Auto-flammability, Explosive and Oxidising Properties) Oct 1992 92/DES081/0866.

H 04. Goebel, G.V. 1985a. Characterization of Radioacativity in bile from rats dosed orally with ^{14}C Fenarimol. May ABC-0312.

H 10. Althaus, W.A. 1985a. Characterization and Identification of Radioactivity in Urine and Feces of Wistar Rates given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0310.

H 11. Althaus, W.A. 1985b. Characterization and Identification of Radioactivity in Blood, Liver, and Kidney of Wistar Rats given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0321.

H 17. McCorquodale, G.Y. and Prout, M.S. 1994. The disposition of [^{14}C]-fenarimol in the lactating goat. DowElanco Ltd., Report No. 10422.

K 25. Dow Elanco Ltd. Rate of Hydrolysis of EL-222.

K 26. Day, E.W. Preliminary Photochemical Studies with the Fungicide EL-222.

K 28. Mosier, J.W. and Saunders, D.G. Photochemical Studies with Fenarimol. Aug 1976.

L 01. Althaus, W.A. Bewley, G.W. Separation and Identification of Degradation Products formed from ^{14}C Fenarimol Applied to Apples. Jan 1978b.

L 02. Althaus, W.A. A Comparative Apple Residue Study Conducted with Carbinol-labelled and mixed-labelled ^{14}C Fenarimol. Mar 1984b ABC-0199.

L 03. Althaus, W.A. ^{14}C Fenarimol Grape Residue Study. Apr 1984 ABC-0237, ABC-0239.

L 04. Goebel, G.V. Isolation and Identification of "Metabolite Complex" from ^{14}C Fenarimol-Treated Grapes Mar 1985 ABC-0316.

L 05. Rainey, D.P. Supplementary Information on Metabolism of ^{14}C Fenarimol in Grapes. Nov 1987 ABC-0239S.

L 08. Althaus, W.A. ^{14}C Fenarimol Residue Study in Cucumbers. Oct 1986. ABC-0307.

L 09. Althaus, W.A. Bewley, G.W14C Fenarimol Apple Residue Study Jan 1978a.

N1 02. Dow Elanco Ltd. Residue Study - Artichoke - Italy 1979 179-251.

NA 06. Althaus, W.A. ^{14}C Fenarimol Chicken Tissue Residue Study. Sept 1982. ABC-0186.

NA 07. Althaus, W.A.^{14}C Fenarimol Chicken Egg Residue Study. Sept 1982 ABC-0147.

NA 09. Althaus, W.A. *et al*. ^{14}C Fenarimol Swine Tissue Residue Study. Apr 1984a. ABC-0202.

NA 10. Koons, J.R. *et al*. Determination of Tissue Residues in Swine and Beef Cattle Fed Diets Containing Fenarimol. Mar 1984 S-AAC-83-04.

NB 01. Dow Elanco Ltd. Residue Study - Cucumber - Austria 1976 A76-106.

NB 02. Dow Elanco Ltd. Residue Study - Melon- France 1976 F76-04.

NB 03. Dow Elanco Ltd. Residue Study-Cucumber-Italy 1976 176-33.

NB 04. Dow Elanco Ltd. Residue Study - Cucumber - UK 1976 FG76-016.

NB 08. Dow Elanco Ltd. Residue Study - Cucumber - Italy 1977 177-234.

NB 09. Dow Elanco Ltd. Residue Study - Cucumber - Italy 1977 177-235.

NB 10. Dow Elanco Ltd. Residue Study - Squash - Italy 1977 177-236.

NB 11. Dow Elanco Ltd. Residue Study - Cantaloupe - Italy 1977 177-251.

NB 12. Dow Elanco Ltd. Residue Study - Watermelon - Italy 1977 177-253.

NB 15. Dow Elanco Ltd. Residue Study - Cucumbers - Italy 1981 181-255.

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NB 20. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-729.

NB 21. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-730.

NB 22. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-730A.

NB 23. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-735.

NB 24. Dow Elanco Ltd. Residue Study - Cantaloup - Italy 1981 181-256.

NB 26. Dow Elanco Ltd. Residue Study - Squash - Italy 1981 181-254.

NB 28. Dow Elanco Ltd. Residue Study - Artichokes - Italy 1981 181-251.

NB 29. Arcas, J.B. Analises de Residuos de Fenarimol em Frutos e Cucurbitaceas 1986.

NB 30. Dow Elanco Ltd. Application for clearance of RUBIGAN systemic Fungicide to the Technical Committee on Agricultural Chemicals Section E-Residues (Australian Data Summary). Undated.

NB 30. Application for clearance of RUBIGAN systemic Fungicide to the Technical Committee on Agricultural Chemicals Section E - Residues, 1979.

NB 31. Butcher, S. Residues in Melons Spain 1994 Jan 1995 GHE-P-4011.

NB 32. Butcher, S. Residues in Melons Italy 1994 Jan 1995 GHE-P-4013.

NC 11. Dow Elanco Ltd. Residue Study - Strawberry - Italy 1979 179-252.

NC 12. Dow Elanco Ltd. Residue Study - Strawberry - Italy 1979 179-253.

NC 16. Rubigan 12 WP/Strawberry Crop Dow Elanco Ltd. Residue Study: Japan 1984 and 1988 Studies June 1988 T2R-077.

ND 01. Longhurst, C Residues of Fenarimol in Raspberries following Foliar Applications of RUBIGAN Sept 1985 FF84-006.

NE 02. Dow Elanco Ltd. Residue Study - Peppers - Spain 1977 E77-129.

NE 03. Dow Elanco Ltd. Residue Study - Tomatoes - Italy 1979 179-251.

NE 04. Dow Elanco Ltd. Residue Study - Peppers - Israel 1979 ISL79-2.

NE 05. Dow Elanco Ltd. Residue Study - Pepper - Italy 1979 179-250.

NE 06. Dow Elanco Ltd. Residue Study - Pepper - Italy 1979 179-251.

NE 07. Dow Elanco Ltd. Residue Study - Tomatoes - Italy 1979 179-250.

NE 08. Butcher, S.M. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12ec (EAF 457), Spain 1993 Aug 1994 GHE-P-3653.

NE 09. Dow Elanco Ltd. Residue Study - Tomatoes - Italy 1981 181-258.

NE 10. Dow Elanco Ltd. Residue Study - Pepper - Italy 1981 181-259.

NE 11. Butcher, S.M. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12SC (EAF 383), Netherlands 1994 Jan 1995
. GHE-P-4008.

NE 12. Butcher, S.M. Residues of Fenarimol in Tomatoes - Greece 1994 Jan 1995
. GHE-P-4012.

NF 03. Dow Elanco Ltd. Residue Study - Pears - Germany 1978 D78-312.

NF 06. Dow Elanco Ltd. Residue Study - Pears - Italy 1981 181-211.

NF 08. Dow Elanco Ltd. Residue Study - Apples - Germany 1978 D78-311.

NF 18. Decker, O.D. and Day, E.W. Fenarimol Residue Data on Apples and Apple Products from Experiments conducted in the United States in 1981 and 1982. Mar 1983. I-ODD-83-06.

NF 20. Dow Elanco Ltd. Residue Studies-Apples Germany and UK/1981 Apr 1983
. D81-302, D81-350, D81-351, D81-353, FF81-002.

NF 21. Dow Elanco Ltd. Residue Studies - Apples Germany 1982 Apr 1983. D82-301, D82-302, D82-303, D82-304, D82-305, D82-307.

NF 25. Frank, R. Fenarimol Residues in Whole Apple Fruit (Canada) May 1977 T2R-233.

NF 26. Frank, R. Fenarimol Residues in Whole Apple Fruit (Canada) July 1978 T2R-198.

NF 27. Day, E.W. Fenarimol Residue Data on Apples from Canada May 1981.

NF 28. Day, E.W. Fenarimol Residues in Apples from Chile May 1981 T2R-230.

NF 29. Day, E.W. Fenarimol Residues in Apples from New Zealand Mar 1981. NZ75-19, NZ78-2, NZ80-5, NZ80-6.

NF 31. Day, E.W. West, S.D 1988 Fenarimol Residue

Studies in Apples Nov 1988. AAC8819.

NF 33. Day, E.W. Fenarimol Residue Data on Pears March 1987 EWD8640.

NG 01. Dow Elanco Ltd. Residue Study - Peach - Italy 1977 177-212.

NG 02. Dow Elanco Ltd. Residue Study - Peach 1977 177-213.

NG 03. Dow Elanco Ltd. Residue Study - Peach - Italy 1977 177-214.

NG 04. Day, E.W and Saunders, D.G. 1987 Fenarimol Residue Studies in Cherries AAC8713 Feb 1988.

NG 05. Day, E.W. and West, S.D. 1989 Fenarimol Residue Studies in Cherries, Aug 1989 AAC8903.

NG 06. Day, E.W. and Saunders, D.G Storage Stability of Fenarimol in Cherries EWD8803 Feb 1988.

NG 07. Butcher, S. and Wood, S. Residues of Fenarimol in Peaches at intevals following Application of RUBIGAN 4 (EAF 216), - Southern France 1993 GHE-P-3652 Aug 1994.

NG 08. Butcher, S. and Wood, S. Residues of Fenarimol in Peaches at intervals following Application of RUBIGAN 12sc (EAF383), Italy - 1993 GHE-P-3626 Jun 1994.

NG 09. Dow Elanco Ltd. Residues in Nectarines in Chile, Gonzalez, R.H Degradacion de Residous de Rubigan en Nectarinos Y Fijacion de Carencias Preliminares Chile 1993.

NG 10. Butcher, S. Peaches Italy Jan 1995 GHE-P-4014.

NG 11. Butcher, S. Peaches France Jan 1995 GHE-P-4062.

NG 12. Butcher, S. The stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditons. GHE-P-4318.

NH 01. Dow Elanco Ltd. Residue Study - Grapes AAC8714.

NH 02. Dow Elanco Ltd. Residues Study - Grapes EWD8703.

NH 04. Butcher, S. and Wood, S. Residues of Fenarimol in Grapes at Intervals following Application of TRANSFLO (EAF 383), France - 1993 GHE-P-3627 Jun 1994.

NH 05. Dow Elanco Ltd. Residue Study - Grape 1977 A77-121.

NH 06. Dow Elanco Ltd. Residue Study - Grape 1977 A77-122.

NH 07. Day, E.W. Jr. and Saunders D.G. Storage Stability of fenarimol and its Metabolites in Grapes and Grape Products. EWD8802 Apr 1988.

NH 09. Dow Elanco Ltd. Residue Study - Grape 1977 177-225.

NH 10. Butcher, S. The Stability of Fenarimol in Fortified Grapes and Wine stored under Frozen Conditions GHE-P-3741 Aug 1994.

NH 11. Butcher, S. and Wood, S. Residues of Fenarimol in Grapes, Grape Must and Wine following Application of Rubigan 12 SC (EAF 383) to Grape Vines Germany 1992/93. GHE-P-3655 Aug 1994.

NH 12. Dow Elanco Ltd. Residues Studies - Grapes - Germany and France 1981/2 Apr 1983.

NH 17. Day, E.W. Fenarimol Residue Data on Grapes and Grape Products from Experiment conducted in the United States in 1983 March 1984 I-EWD-84-03.

NH 20. Day, E.W. and West, S.D. 1988 Fenarimol Residue Trials in Grapes AAC8818 Dec 1988.

NH 22. Trevallyn-Jones, J. Further Submission to T.C.A.C - Withholding Period in Grapes treated with RUBIGAN (contains Australian Dow Elanco Ltd. Residue data) July 1984.

NH 23. Dow Elanco Ltd. Submission to T.C.A.C - Rubigan Data Supporting Reduction in Withholding Period in Grapes (contains Australian Residue data) July 1987.

NH 24. Dow Elanco Ltd. 1995. Residues of fenarimol in fresh and processed grapes after treating Cabernet Sauvignon and Sultana grapevines with Rubigan 120 EC®. March. Ref.

NI 01. Dow Elanco Ltd. Residue Study - Artichoke - Italy 1979 179-250.

NI 05. Butcher, S. Residues of Fenarimol in Globe Artichokes at Intervals following Multiple Applications of RUBIGAN 12 SC (EAF383), Italy 1995 GHE-P4010 Jan 1995.

NJ 01. Butcher, S. and Perkins, J. Residues of fenarimol in Hops and related fractions from the brewing process following application of Drawisan 6WP (EAF 219) - Germany 1990. GHE-P-2517 Oct 1991.

NL 02. Catta-Preta, R.F. and Matos, J.C. Residues of Fenarimol and its Major Metabolites in Bananas following Multiple treatments with Rubigan Ec Fungicide - Costa Rica, Honduras and Ecuador, 1992 April 1993 GHB-P 151.

NL 03. Ishikura, H. Residues of Fenarimol in Pulp, Peel and Whole Bananas Following application of Rubigan 12EC Fungicide in the Philippines - 1991 July 1991. GHF-P -1126.

NL 04. Day, E.W. Reasonable Grounds in Support of the

Petition for the Establishment of A Tolerance for Fenarimol and its Metabolites in or on Bananas. Aug 1993. ECL93073.

NM 01. Decker, O.D. Fenarimol Residues on Pecans when Rubigan 1EC or Rubigan 1AS is Foliar applied to Pecan Trees on Disease Control March 1983 I-ODD-82-02.

NM 02. Decker, O.D. Fenarimol Residues on Pecans when Rubigan is Foliar applied to Pecan Trees for Disease Control Feb 1984 I-ODD-84-01.

OR 01A. Griggs, R.D and Decker, O.D. Determination of Fenarimol in Agricultural Crops and Soil Jan 1981 AM-AACA-R039-AA-755.

OR 01B. Griggs, R.D. and Decker, O.D. Determination of Fenarimol in Agricultural Crops and Soil Jan 1985 AM-AA-CA-RO39-AB-755.

OR 10. Dow Elanco Ltd. Determination of EL-222 in Agricultural Crops and Soils by Gas-Liquid Chromatography Std An.Method No.86 Sep 1976.

OR 11. Dow Elanco Ltd. Determination of Fenarimol In Agricultural Crops (Other than Cereals) by Gas-Liquid Chromatography Nov 1977 Std.An.Method No.97.

OR 19. Yordy, D.W. and Turner, L.G Determination of Fenarimol In Meat, Milk and Eggs. AM-AA-CA-RO72-AA-755 Sep 1982.

OR 20. Butcher, S.M. and Perkins, J.M. Determination of Fenarimol Residues in Fresh, Dried and Spent Hops. ERC91-8 Jan 1992.

OR 21. Butcher, S.M. Determination of Fenarimol Residues in Beer and Spent Yeast. Jan 1992 ERC91-10.

OR 22. Butcher, S.M. and Long, T.J. Determination of Residues of Fenarimol in Grape Must, Wine and Grapes. ERC93-6 Jul 1993.

OR 24. Butcher, S.M. Determination of Residues of Fenarimol in Tomatoes, Peaches and Melons ERC 94.3 Aug 1994.

OR 27. Turner, L.G. Dow Elanco Ltd. Residue Method Development Report for Fenarimol and its Metabolites in Whole Bananas and Banana Pulp. GH-C-2840 Aug 1992.

R 28. Catta-Preta, R.F. and Matos, J.C Determination of Residues of Fenarimol, Compound 212746 and 210302 in Banana Whole Fruit and Pulp BRC 92.2 March 1993.

FENARIMOL (191)

IDENTITY

ISO common name: fenarimol

Chemical name

IUPAC: (±)-2,4′-dichloro-Æ-(pyrimidin-5-yl)benzhydryl alcohol

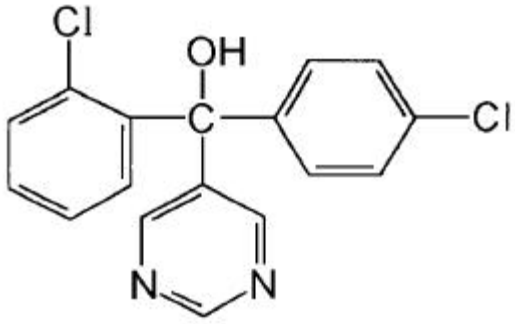
CA: (±)-Æ-(2-chlorophenyl)-Æ-(4-chlorophenyl)-5-pyrimidinemethanol

CAS registry no: 60168-88-9 (unstated stereochemistry)

CIPAC No: 380

Synonyms: compound 57322
development code EL-222

Structural formula:



Molecular formula: $C_{17}H_{12}Cl_2N_2O$

Molecular weight: 331.2

Physical and chemical properties

Pure active ingredient

Vapour pressure:	6.5×10^{-5} Pa at 25°C (99.7% pure) (A 21)	
Hydrolysis (no purity stated):	pH 3	no hydrolysis
(Dow Elanco Ltd., undated)	pH 6	no hydrolysis at 25, 37 and 52°C
	pH 9	no hydrolysis
Following 40 hours reflux at 100°C:	pH 3	30% hydrolysis
	pH 6	no hydrolysis
	pH 9	13% hydrolysis

Photolysis (no purity stated):

Sunlight or simulated sunlight

half-life in 2 mg/l water solution in summer sun: 12 hours
half-life in water in laboratory simulated sunlight: <1 hour
half-life on silica gel plates in sunlight: approx 14 hours (Day, undated)

Laboratory irradiation apparatus
half-life in distilled water: 0.6 hours
half-life in 2% acetone/water: 2.0 hours (Mosier and Saunders, 1976)

No information was submitted for the pure active ingredient on melting point, octanol/water partition coefficient, solubility or specific gravity.

Technical material

Purity:	Typically ≥97% with certified limits of 95-101% to allow for assay and production variability. Impurities <0.5%. except for the 2,2′-, 2,3′- and 4,4′-dichloro isomers of fenarimol (total max. 3%) (Day, 1985)
Colour:	off-white to buff (Day, 1984)
Physical state:	crystalline solid (Day, 1984)
Odour:	slightly aromatic (Day, 1984)
Melting point:	117-119°C (Day, 1984)
Octanol/water partition coefficient:	Log K_{ow} = 3.69 (Loh, 1976, Day, 1984)

Solubility
(mg/l at 25°C; purity was either 95.4% or unspecified)

water at pH 3	14.6
water at pH 7	13.7
water at pH 10	13.8
acetone	>250
acetonitrile	40-45
benzene	100-125
chloroform	>500
cyclohexanone	>500
ethyl cellosolve	>250
heavy aromatic naphtha	40-45
hexane	1.1
methanol	100-125
methyl cellosolve	>250
xylene	40-45 (Day, 1976, 1984)

Specific gravity:
Packed bulk density: 0.7 - 0.8 kg/m^3
Loose bulk density: 0.4 kg/m^3 (Hudson, 1987; Day, 1984)

Formulations

Fenarimol is formulated mainly as either WP, EC or SC products.

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Rats. [^{14}C]fenarimol was extensively metabolized in wistar rats with less than 3% of the dose excreted unchanged in the urine and faeces within 7 days, and with only trace amounts being detected in the bile. More than 40 metabolites, each representing only a small fraction (<10%) of the dose, were detected in the urine and faeces. Some 10 metabolites were tentatively identified by a combination of thin-layer chromatography/autoradiography, mass spectrometry, infrared spectrometry and nuclear magnetic resonance spectrometry. Many metabolites appeared to be common to both the urine and faeces. The proposed major metabolic pathways of fenarimol are oxidation of the carbinol-carbon atom, the chlorophenol rings and the pyrimidine ring, as shown in Figure 1. A proposed minor metabolic pathway involves cyclization between a chlorophenol ring and the pyrimidine ring (Goebel, 1985a; Althaus, 1985a).

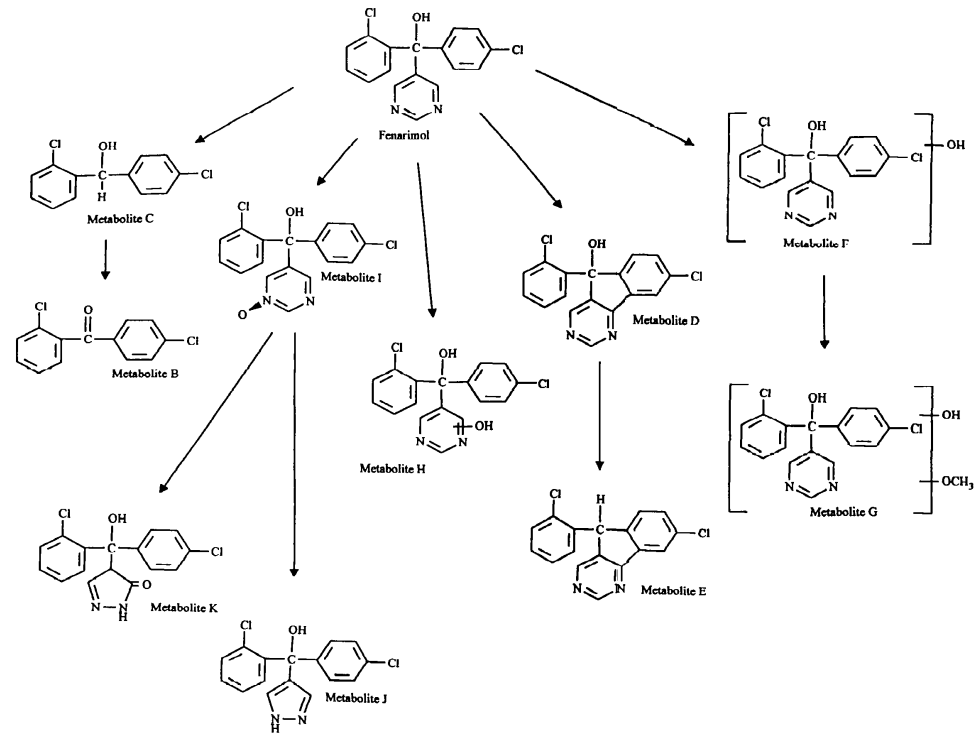
Biliary metabolites existed predominantly as glucuronic acid conjugates, with similar metabolite profiles being seen at both the dose levels tested. The main metabolite present in bile after enzymatic hydrolysis was 4-[(2-chlorophenyl)(4-chlorophenyl)hydroxymethyl]-3-pyrazolone (metabolite K, Figure 1). In contrast, most of the radioactivity in the faeces was present as unconjugated compounds indicating that biliary metabolites undergo further metabolism or hydrolysis before being eliminated (Goebel, 1985a).

In a further study rats were dosed with a single oral dose of 1 or 13 mg/kg [^{14}C]fenarimol. The major radiolabelled constituents identified in the blood and kidneys 1 hour after dosing were unchanged fenarimol and fenarimol *N*-oxide (metabolite I); fenarimol predominated, except in the blood of low-dose males, as shown in Tables 1 and 2. Identification was by thin-layer chromatography. Fenarimol also accounted for most of the radioactivity in the liver 1 h after dosing (Table 3). In addition 3-6% of the radioactivity in the liver was tentatively identified as 4-[(2-chlorophenyl)(4-chlorophenyl)hydroxymethyl]-3-pyrazolone (metabolite K) (Althaus, 1985b).

Table 1. Major compounds in whole blood of male and female rats.

Blood	Dose, mg/kg	% of total ^{14}C	% of ^{14}C in blood		
			Fenarimol	Fenarimol *N*-oxide	Other
Male	1	0.152	19.3	41.3	39.4
Female	1	0.126	49.5	21.8	28.7
Male	13	1.154	40.4	36.7	22.9
Female	13	1.804	72.5	10.9	16.6

Figure 1. Proposed metabolic pathways of fenarimol in rats.



Metabolite Metabolite F: Three isomers observed. One isomer was hydroxylated in the 4-position of the 2-chlorophenyl ring and was confirmed by synthesis of the authentic model compound. The positions of the ring hydroxyl group in the other two isomers are unknown.

Metabolite G: This compound contains hydroxy and methoxy groups. Their positions are unknown.

Metabolite H: The position of the hydroxyl group on the pyrimidine ring is unknown.

Table 2. Major compounds in kidneys of male and female rats.

Kidneys	Dose, mg/kg	Fenarimol, %	Fenarimol *N*-oxide, %	Other, %
Male	1	48	19	32
Female	1	66	11	23
Male	13	64	15	21
Female	13	84	5	11

Table 3. Major compounds in liver of male and female rats.

Liver	Dose, mg/kg	Fenarimol, %	Metabolite K, %	Other, %
Male	1	67	6	27
Female	1	82	5	13
Male	13	77	6	17
Female	13	90	3	7

Goats. A lactating goat (breed unspecified) was dosed twice daily for 5 days with gelatine capsules containing [carbinol-^{14}C]fenarimol at a dose equivalent to 10 ppm in the diet and killed sixteen hours

after the final dose.

The radioactivity of tissue samples was determined by combustion/LSC. The chromatographic profiles of samples were determined by radio-TLC following preparation which generally involved an acidification and purification on a C18 column eluted with methanol. Flash chromatography was used to prepare some samples. Samples of protease-digested livers were also obtained. Further identification was carried out by HPLC with UV detection and/or GC-MS. Eighty two per cent of the total dose was excreted by the end of the study (urine 28%, faeces 53%, cage wash 0.7%, milk <0.1%). The tissues and gut contents accounted for 16% of the total dose. The maximum plasma concentration occurred 97 hours after the first dose (0.034 mg/l fenarimol equivalents) which coincided with the maximum concentration in whole blood (0.03 mg/l fenarimol equivalents) indicating that binding to red blood cells was not taking place. The maximum concentration in the milk occurred 80 hours after the first dose (0.08 mg/l fenarimol equivalents). The radioactivity in other compartments was distributed as shown in Table 4.

Table 4. Radioactivity in a goat dosed with [^{14}C]fenarimol.

Sample	mg/kg fenarimol equivalents	% of total dose
Bile	2.97	0.1
GI tract	0.18	0.82
GI tract contents	0.94	12.2
Carcase	0.02	2.0
Fat - omental	0.03	-
Fat - renal	0.03	-
Fat - subcutaneous	0.03	-
Kidneys	0.14	0.04
Liver	0.42	0.7
Muscle	0.01	0.1

At least 90% of the total radioactivity in muscle and fat samples was extractable. The compounds shown in Table 5 were identified.

Table 5. Extraction efficiency and metabolites detected in goats (% of radioactivity present).

Compounds[1]	Sample						
	Liver		Kidney		Faeces, %	Urine, %	Bile, %
	%[2]	mg/kg[3]	%	mg/kg			
Compound 1 + Compound 2	34	0.14	38	0.05	36	87	93
fenarimol	-		-		9	-	3
fenarimol + 2-chlorobenzoic acid	21	0.09	11	0.02	-	-	-
2-chlorobenzoic acid + 4-chlorobenzoic acid + dehydroxyfenarimol	-		-		9	--	
4-chlorobenzoic acid + dehydroxyfenarimol	-		4		-	-	-
Unidentified	40		43		42	0	3
Numer of unidentified compounds	4		3		3	0	1
Extractable ^{14}C as % of ^{14}C in sample	69		94		61	100	85

[1] See Figure 2
[2] Of extracted ^{14}C in sample
[3] Fenarimol equivalents

The presence of compounds 1 and 2 in liver, kidney and bile could not be confirmed with a second solvent system but was confirmed in faeces and urine.

Further characterization was attempted using protease-digested liver but no results were obtained owing to the low levels of radioactivity. GC-MS of the liver extract indicated the possible presence of a fenarimol methyl sulphone derivative (which may arise as a result of glutathione conjugation, thio-ether cleavage, methylation and oxidation) (McCorquodale & Prout, 1995).

Pigs. Three cross-bred pigs were dosed twice daily for 5 days by incorporation of labelled fenarimol (>99% radioch;emical purity) into the feed at a level of 1 ppm (dry matter). One pig was dosed with [*carbinol*-^{14}C], one with [2-*chlorophenyl*[^{14}C] and the third with [4-*chlorophenyl*-^{14}C]fenarimol. The animals were killed 6-7 hours after the final feed. The radioactivity of the samples was determined by combustion and/or LSC. Results are shown in Table 6.

Table 6. Total residues in pig tissues following dosing with [^{14}C]fenarimol (all label positions)

Sample	mg/kg fenarimol equivalents	LSC recovery from spiked samples (%)
Liver	0.19-0.24	106, 141
Kidney	0.05-0.06	114, 127
Fat	0.04-0.06	-
Muscle	0.01	105, 140

Liver samples were extracted with methanol and dichloromethane/sodium chloride solution and analysed by TLC with autoradiography following purification by column chromatography (silica gel eluted with toluene/ethyl acetate and methanol). Fat samples were extracted with "hexanes" and acetonitrile, and the ^{14}C measured by LSC. The distribution of radioactivity in various extracts was as shown in Table 7.

Table 7. Distribution of radioactivity in sample extracts.

Sample/fraction	Position of radiolabel/% of total ^{14}C in sample		
	carbinol	2-chlorophenyl	4-chlorophenyl
Liver			
unextracted	23	35	20
dichloromethane extract	65	57	68
aqueous extract	13	18	12
Fat			
acetonitrile extract	88	85	90
"hexanes" extract	12	14	10

The major compound in the dichloromethane extracts of liver and the acetonitrile extracts of fat was fenarimol, accounting for 41-43% of the total radioactivity in the liver and 90% of the total in the fat (Althaus *et al*., 1984).

Chickens. Eight chickens (Hubbard x White Mountain Cross) were fed for 5 days with a diet containing 0.7 or 7 ppm [*carbinol*-14C]fenarimol (radiochemical purity 99.8%) and killed within one hour of removing the feed. The radioactivity of the samples was determined by combustion and LSC, with the results shown in Table 8 (Athaus *et al*., 1982a).

Table 8. Radioactive residues in chicken tissues following dosing with [^{14}C]fenarimol.

Sample	Assay recovery (%)	mg/kg fenarimol equivalents	
		0.7 ppm diet	7 ppm diet
Liver	109	0.01-0.013	0.113-0.12
Kidney	126	0.005-0.006	0.06-0.07
Fat	91	0.001-0.002	0.02-0.05
Skin	90	0.001-0.002	0.02
Muscle	113	0.001	0.003-0.005

In a second study, six Leghorn hens were dosed for 7 days with a feed containing 0.6 ppm [*carbinol*-^{14}C]fenarimol (radiochemical purity >99%) and then for a further 23 days with untreated feed. Eggs were collected daily, bulked to form a composite sample and analysed by LSC. Assay recoveries were 86.0-98.6%. The highest level of radioactivity was detected in day 7 samples (0.003 mg/kg fenarimol equivalents). By day 10 (3 days after the final treated feed) the radioactivity had decreased to 0.001 mg/kg, and was equivalent to background levels by day 17 (10 days after withdrawing treated feed) (Althaus, 1982b).

Plant metabolism

Apples. [*Carbinol*-^{14}C]fenarimol (radiochemical purity >99%) was formulated as an emulsifiable concentrate and diluted to give a 40 mg/l aqueous emulsion. This was applied as a spray to apple trees (Jonathan). The location of the trials was unspecified. Applications were made to run-off (2-5 litres aqueous emulsion/tree/application) at 80% full bloom (unlabelled formulation), 80% petal fall and on nine other occasions (radiolabelled formulation) at one- to two-week intervals (equivalent to 80-200g ai/ha based on a planting density of 1000 trees/ha). The total radioactivity was determined by combustion/LSC. The distribution of radioactive residues is shown in Table 9.

Table 9. Distribution of radioactive residues in apples.

Time after spraying	Whole apple	Peel		Pulp	
	mg/kg fenarimol equivalents	% of ^{14}C in whole apple	mg/kg fenarimol equivalents	% of ^{14}C in whole apple	mg/kg fenarimol equivalents
6 hours	0.207	92	0.983	9	0.023
29 days	0.108	87	0.477	13	0.019
49 days	0.074	81	0.351	19	0.017

Samples were extracted with methanol/sodium chloride solution and dichloromethane, then analysed by TLC/LSC. The distribution of radioactivity in the extracts and the fenarimol content were as shown in Table 10.

Table 10. Distribution of radioactivity and fenarimol in apple extracts (mean of 2 trees).

Sample	% of ^{14}C in sample	[^{14}C]fenarimol in sample

	aqueous phase	dichloromethane extract	unextracted	% of total ^{14}C	mg/kg sample
6 hour peel	10.8	67.9	21.4	53	0.52
29 day peel	13.9	47.6	38.6	24	0.18
49 day peel	15.7	44.8	39.5	23	0.14
49 day pulp	57.7	32.5	9.9	18	0.003

The authors of the study state that radioactivity other than that from fenarimol, equivalent to 0.06 mg/kg fenarimol on a whole-apple basis in the 49-day peel samples, was "widely distributed between many compounds".

Samples of peel obtained 52 days after the final application were also taken to attempt to identify metabolites. The samples were refluxed with methanol/2N sodium hydroxide solution and then partitioned successively with dichloromethane and butanol. These extracts were analysed by LSC or purified by column chromatography (silica column eluted with methanol/water). Analysis was by TLC with detection by UV and/or autoradiography and comparison with photodegradation products. Following extraction, the radioactivity was distributed as shown in Table 11.

Table 11. Distribution of radioactive residues in peel fractions.

Fraction	% of peel radioactivity	mg/kg fenarimol equivalents
spent peel (after refluxing)	17.2	0.24
dichloromethane extract	50.9	0.70
butanol extract	26.4	0.36
aqueous phase	5.5	0.08

Several compounds were tentatively identified by comparison with photolysis products (photoproducts A, E, D and H, Figure 2), all at ≤1% of total radioactivity or ≤0.01 mg/kg fenarimol equivalents. The authors concluded that photochemical degradation occurred on the surface of the apple. Other compounds (including >40 which were very polar) were observed but not identified. They had similar chromatographic characteristics to photodegradation products (Althaus and Bewley, 1978a,b).

In a further study carried out in Chile radiolabelled fenarimol was formulated as emulsifiable concentrates, diluted to give 1000 mg/l aqueous emulsions and applied directly as a mist spray to apples (Starkrimson). Radiolabelling was either at the carbinol carbon or mixed carbinol and both chlorophenyl rings (radiochemical purity 99.5-99.9%).

Individual apples were sprayed with 1 ml of the formulation or to run-off (whichever occurred first). This rate is equivalent to 268 kg ai/ha based on an average yield of 30t/ha and a medium-sized apple weighing 112g. Samples were taken 14 days after application and separated into pulp and peel.

Peel samples were extracted with aqueous methanol and dichloromethane, then refluxed with 2-butanol/water before partitioning between dichloromethane and aqueous methanol. Analysis was by TLC with autoradiography and LSC. The distribution of radioactive residues was as shown in Table 12.

Table 12. Distribution of radioactive residues in apple peel extracts.

Sample	[^{14}C]carbinol		mixed label ^{14}C	
	% of radioactivity	mg/kg fenarimol equivalents	% of radioactivity	mg/kg fenarimol equivalents
First dichloromethane	84	3.4	86	4.2
First aqueous	3	0.1	5	0.24
Second dichloromethane	3	0.1	3	0.15
Second aqueous	1	0.04	1	0.05
Unextractable	9	0.4	5	0.24
Total	100	4.0	100	4.9

Pulp samples were found to contain *c.* 0.06 mg/kg fenarimol equivalents in both experiments. TLC and LSC of peel samples identified *c.* 65% of the ^{14}C from both labels as the parent (*c.* 3 mg/kg).

No differences were detected between the TLC autoradiographs from the two radiolabels. No major degradation product was detected. Individual degradation products accounted for 2% of the total radioactivity, and all those identified in the peel were present as photolysis products. Small amounts of the major photolysis product *o*-chlorobenzoic acid were detected (Althaus, 1984a).

Grapes. A mixture of [*carbinol*-^{14}C], [*4-chlorophenyl*-^{14}C] and [*2-chlorophenyl*-^{14}C]fenarimol was formulated as an emulsifiable concentrate and diluted to give 120 mg/l and 500 mg/l aqueous emulsions. These were applied as foliar sprays to grapes (Ribier) four times at two-week intervals (120 mg/l formulation; total dose equivalent to 0.166 kg ai/ha) or once (500 mg/l formulation; dose unspecified). Samples were collected 0, 15, 30, 45 and 60 days after the final treatment.

Samples from the multiple-treatment study were extracted with methanol and partitioned with dichoromethane. The spent grape residue was extracted with 2-butanol-water by Soxhlet. The distribution of radioactivity was as shown in Tables 13 and 14.

Tables 13 and 14. Distribution of radioactivity in grapes following multiple applications of [^{14}C]fenarimol.

Table 13.

Days after final application	Total radioactivity as mg/kg fenarimol	% of total radioactivity			
		Dichloromethane	Aqueous	Butanol	Remainder
0	0.66	67.5	l6.8	8.5	7.2
15	0.46	63.6	15.2	11.7	9.5
30	0.33	61.6	16.1	8.1	14.3
45	0.33	59.8	16.8	9.0	14.4
60	0.19	56.4	18.2	11.1	14.3

Table 14.

Days after final application	TLC of dichloromethane fraction					
	Fenarimol		"Metabolite complex"		Unidentified	
	%[1]	mg/kg	%[1]	mg/kg[2]	%[1]	mg/kg[2]
0	46.0	0.305	12.7	0.08	8.8	0.06
15	26.9	0.124	26.5	0.12	10.2	0.05
30	19.3	0.063	29.1	0.10	13.2	0.04
45	17.8	0.058	27.9	0.09	14.1	0.05
60	15.6	0.029	26.5	0.05	14.3	0.03

[1] Of total radioactivity in Table 13
[2] Fenarimol equivalents

Samples taken 60 days after the single application were extracted into acidic water, refluxed with neutral, basic or acidic aqueous methanol, combined with sodium chloride solution, partitioned with dichloromethane, and then further partitioned with neutral, basic or acidic dichloromethane.

Neutral and acidic dichloromethane extracted 61 and 67% of the total radioactivity respectively. The extracts contained fenarimol and "metabolite complex" (which was not identical in different extracts). The term "metabolite complex" was applied to a group of two major, one minor and several trace components which were "extractable in the non-polar organic solvents , but which possessed polar adsorption chromatographic properties."

After extraction under strongly basic conditions the dichloromethane phase contained 74% of the total radioactivity but did not contain significant amounts of "metabolite complex".

Three compounds were identified: fenarimol (20%), dehydroxyfenarimol (DHF, 22%) and 2,4′-dichlorobenzophenone (DCBP, 8%). The structures of these compounds are shown in Figure 2 below. The "metabolite complex" was thermally degraded when subjected to GLC or MS, degraded by aqueous hydrolysis, and bound strongly during HPLC (Althaus, 1984b).

Further studies were conducted to identify the components of the "metabolite complex". Grape samples were refluxed with methanol/water, the extract was diluted with aqeous NaCl solution and extracted with dichloromethane. After drying, the residue was reconstituted in aqueous methanol and sequentially partitioned with hexane, chloroform/trichloroethane, and dichloromethane. The distribution of radioactivity was as shown in Table 15.

Table 15. Composition of grape extracts after sequential partitioning.

Solvent	% of radioactivity extracted as				
	Fenarimol	"Metabolite complex"[1]			Total
		Zone A	Zone B	Zone C	
Hexane	1-2	0	0	0	2
80:20 Chloroform/trichloroethane	18	3	1	1	27
50:50 Chloroform/trichloroethane	0.5	6	3	2	15
Dichloromethane	<0.5	1	5	2	9
Total	*c.* 20	10	9	5	53

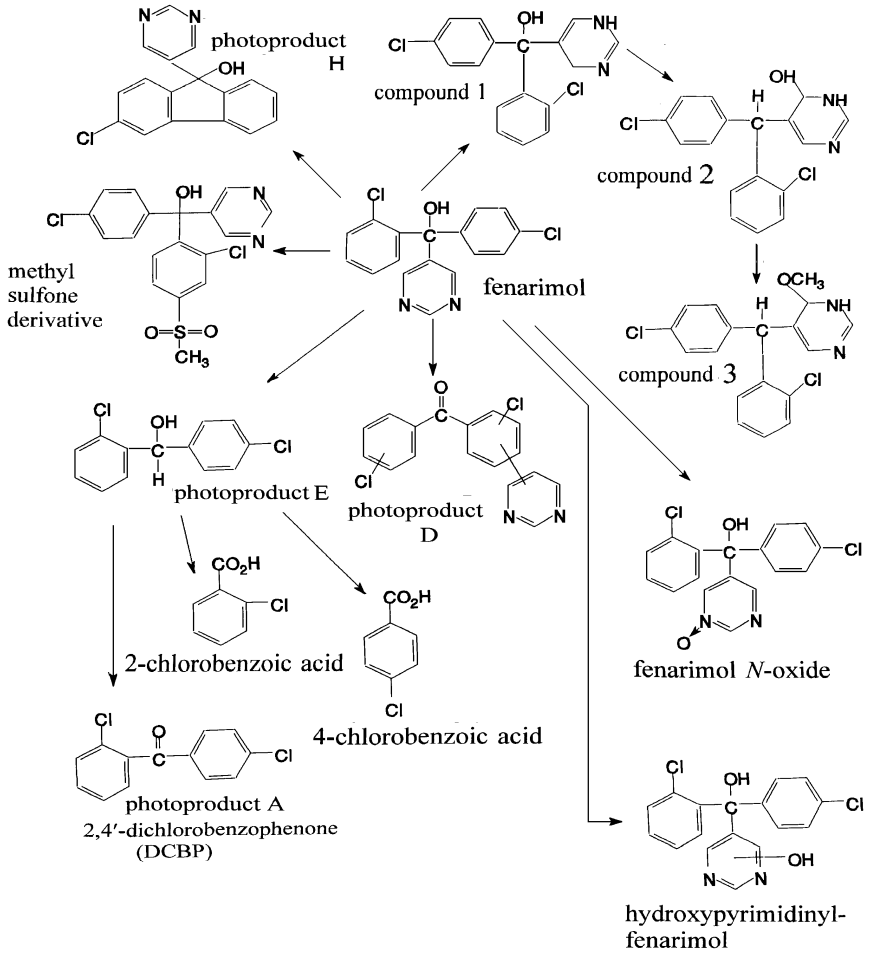
[1] Zones refer to retention on TLC plate. Zone C most polar, Zone A least polar.

The 50:50 chloroform/trichloroethane and the dichloromethane fractions were subjected to further aqueous/methanolic sodium hydroxide hydrolysis when *c.* 50% of the extracted radioactivity was attributed to dehydroxyfenarimol (DHF) and 2,4′-dichlorobenzophenone (DCBP). The dehydroxyfenarimol was apparently produced during the hydrolysis.

Further analytical investigations of the "metabolite complex" in the basic extract were carried out using radio-HPLC, NMR and MS.

Compound 3 (Figure 2) was tentatively identified by MS but could not be confirmed by NMR, owing to the small quantity obtained. Compound 1 was tentatively identified by MS. Positions of reduction of the pyrimidine ring were investigated using NMR. Compound 2 was tentatively identified by MS but there was too little for confirmation by NMR. Three isomeric structures could exist (where -H and -OH have been added to the pyrimidine ring). The hypothesis that compound 1 could be converted to compound 2 under acidic conditions and subsequently to compound 3 by methanolysis under acidic conditions was proposed.

Figure 2. Proposed pathways of metabolism in livestock and plants, and of potodegradation.



In further work to characterize other metabolites in grapes, it was concluded that the unidentified radioactivity was associated with many minor components (34 "zones" were isolated). No individual component accounted for more than 2.9% of the total radioactivity (0.04 mg/kg fenarimol equivalents) (Goebel, 1985b; Rainey, 1987).

Cucumbers. [*Carbinol*-^{14}C]fenarimol was formulated as an emulsifiable concentrate and diluted to give a 26.5 mg/l aqueous emulsion. It was applied as a spray to field-grown cucumbers (Green Prolific) in the USA. One application was made to run-off at a rate equivalent to 24.7g [^{14}C]fenarimol in 934 litres water/ha. Samples were taken four days after treatment and analysed by combustion and/or LSC. The characterization of metabolites was carried out by radio-TLC.

After extraction by refluxing with methanol and further extraction with dichloromethane the total radioactivity in the crop ranged from 0.003 to 0.042 mg/kg fenarimol equivalents. Approximately 93% of this (0.04 mg/kg fenarimol equivalents) was extracted into dichloromethane and 85% of the extracted radioactivity (0.03 mg/kg fenarimol equivalents) was attributed to fenarimol and 8% (0.003

mg/kg fenarimol equivalents) remained at the origin. Three other chromatographic bands were separated, each accounting for 3% of the radioactivity (0.001 mg/kg fenarimol equivalents) (Althaus, 1986).

Environmental fate in soil and water/sediment systems

No data were submitted.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Methods for the analysis of a wide range of samples were supplied. In all of these the final determination is by GLC of a toluene solution, with EC detection. Validation data are shown in Table 16.

Crops and soil. Samples were extracted with ethanol/acetone, partitioned into chloroform, dissolved in toluene and analysed by GLC with an ECD. No validation data were submitted (Dow Elanco Ltd., 1976).

Crops other than cereals. Samples were extracted with methanol, partitioned into dichloromethane and transferred to toluene for analysis. No validation data were submitted (Dow Elanco Ltd., 1977).

Fresh fruit and vegetables, pomace, raisins, juice, bananas and "other crops". Samples were extracted with methanol, methanol/water or dichloromethane, then purified by chromatography on an alumina column which was eluted with 1-chlorobutane/methanol. The extract was evaporated and the residue dissolved in toluene for analysis. The authors state that the procedure "usually gives recoveries in excess of 90%" and has a limit of detection of 0.02 mg/kg except in dry pomace and "other crops" where the limit of detection is 0.01 mg/kg. No other validation data were submitted (Griggs and Decker, 1981).

Animal feeding-stuffs (hay and straw). Samples were extracted with methanol/water then purified by chromatography on an alumina column, which was eluted with 1-chlorobutane/methanol, before transfer to toluene (Griggs and Decker, 1985).

Beer. Samples were combined with sodium hydrogen carbonate solution, and partitioned into toluene for analysis (Butcher, 1992).

Spent yeast. Samples were extracted with methanol and, after dilution with water, partitioned with toluene. The extract was concentrated to dryness and the residue dissolved in 30:70 acetonitrile/water, then cleaned up on a C18 column eluted with 50:50 acetonitrile/water, acidified and partitioned into toluene (Butcher, 1992).

Fresh, dried and spent hops. Samples were extracted with methanol and sodium hydrogen carbonate solution and partitioned into methyl isobutyl ether. The extract was treated with alkaline permanganate, partitioned into toluene, dissolved in 1-chlorobutane, and cleaned up on an alumina column eluted with methanol/1-chlorobutane and on a C18 column eluted with acetonitrile/water. After acidification, the extract was partitioned into toluene for analysis (Butcher and Perkins, 1992).

Grape must, wine, grapes, tomatoes, peaches and melons. Samples were extracted with methanol and sodium hydrogen carbonate solution, partitioned into toluene, transferred to dichloromethane and

cleaned up on a C18 column eluted with methanol/dichloromethane or on a silica extraction column eluted with methanol/dichloromethane. The solvent was evaporated and the residue dissolved in toluene for analysis by capillary GLC (Butcher and Long, 1993; Butcher, 1994a).

Soil. Samples were extracted with methanol/water and cleaned up by column chromatography on alumina. Elution was with 1-chlorobutane/methanol. The authors state that the procedure "usually gives recoveries in excess of 90%" and has a limit of detection of 0.02 mg/kg. No other validation data were submitted (Griggs and Decker, 1981,1985).

Banana and banana pulp. Samples were ground with liquid nitrogen, then refluxed in methanol/HCl. NaOH was added to the hot solution which was then allowed to cool. The extract was partitioned with hexane and the hexane fraction washed through sodium sulphate, then evaporated to dryness. The residue was redissolved in toluene and analysed on a 2% OV 17 column. The compounds I and II (Figure 2) are also be determined by this method as dehydroxyfenarimol (Turner, 1992).

In a development of this method the methanol from the reflux solution was evaporated after the addition of NaOH. The remaining aqueous solution was extracted with dichloromethane, which was evaporated and the residue reconstituted in aqueous sodium chloride solution and partitioned with diethyl ether. The ether was evaporated and toluene added. The toluene extract was cleaned up on a silica solid-phase extraction column with elution with 10% ethyl acetate in dichloromethane. After evaporation the reconstituted toluene extract was analysed as above (Catta-Preta and Matos, 1993).

Wildlife. Meat and egg samples were extracted with methanol/acetonitrile or methanol and methylene chloride. Fat was extracted with hexane/1-chlorobutane and milk with acetonitrile, which was washed with hexane and partitioned with methylene chloride. Extracts were cleaned up on a Florisil column, eluted with methylene chloride/methanol, and dissolved in toluene (Yordy and Turner, 1982).

Table 16. Validation of analytical methods (treated plants, plant products, foodstuffs and feeding-stuffs).

Substrate	Spike, mg/kg % recovery	Precision-repeatability	Limit of determination, mg/kg	Reference
Whole apple fruit	0.001-0.02 73-98	no data	0.002-0.003	OR 1B
Dried apple pomace	0.005-0.1 65-103	no data	0.01	OR 1B
Whole fresh grapes	0.001-0.02 100-110	SD + 1-10	0.002-0.003	OR 1B
Wine	0.001-0.02 101-123	SD $\pm$ 2-14	0.002-0.003	OR 1B
Wine	0.01-0.1 99-107	RSD 2.5%	0.01	OR 22
Beer	0.01-0.1 90-108	RSD 4.0%	0.01	OR 21
Spent yeast	0.01-0.1 77-105	RSD 9.7%	0.01	OR 21
Dried hops	0.1-5 78-108	RSD 10.1%	0.1	OR 20
Fresh hops	0.1-2 75-94	RSD 7.4%	0.05	OR 20
Spent hops	0.02-0.5 75-102	RSD 8.3%	0.02	OR 20

Substrate	Spike, mg/kg % recovery	Precision-repeatability	Limit of determination, mg/kg	Reference
Tomatoes	0.01-0.1 86-101	RSD 5.1%	0.01	OR 24
Peach flesh	0.01-0.1 82-117	RSD 9.3%	0.01	OR 24
Melon peel	0.01-0.1 93-109	RSD 5.0%	0.01	OR 24
Melon pulp	0.01-0.1 81-112	RSD 10.2%	0.01	OR 24
Meat	0.01 101	SD ± 16.5	0.01	OR 19
Liver	0.01 108	SD ± 11.5	0.01	OR 19
Kidney	0.01 105	SD ± 13.7	0.01	OR 19
Fat/skin	0.01 87	SD ± 9.1	0.01	OR 19
Milk	0.001 95	SD ± 16.4	0.01	OR 19
Eggs	0.01 98	SD ± 9.0	0.01	OR 19
Banana	0.005-1.0 84-114	no data	0.01	OR 27
Banana pulp	0.005-1.0 82-105	no data	0.01	OR 27
Banana	0 005-1.1 55-114	no data	0.01	OR 28
Banana pulp	0.01-0.53 54-110	no data	0.01	OR 28

Stability of pesticide residues in stored analytical samples

Samples of grapes and wine were fortified with 0.1 mg/kg or mg/l fenarimol and stored deep frozen at -10°C to -27°C up to 370 days. Residues following storage and corrected for procedural recoveries were as shown in Table 17 (Butcher, 1994b).

Table 17. Residues in grapes and wine following storage at -20°C.

Storage period (days)	Residues, mg/kg			
	Black grapes	White grapes	Red wine	White wine
0	0.10-0.11	0.10-0.11	0.09-0.10	0.10
86	0.10-0.11	0.10-0.11	0.10-0.11	0.10
370	0.09-0.10	0.09-0.10	0.09-0.10	0.08-0.11

Ground fresh grapes and grape pomace were fortified with fenarimol at 0.05 mg/kg, and ground raisins and raisin waste at 0.2 mg/kg. Following 14 days refrigeration at 4°C, the samples were stored frozen for an additional 50-119 days. Samples were analysed after 0, 1, and 14 days and at the end of the study. Residues following storage and corrected for procedural recoveries were as shown in Table

18 (Day and Saunders, 1988a).

Table 18. Residues in fresh grapes, wet pomace, raisins and raisin waste following refrigeration and freezer storage.

Storage period, days	Residues, mg/kg			
	Fresh grapes	Wet pomace	Raisins	Raisin waste
0	0.054	0.054	0.20	0.19
1	0.052	0.055	0.18	0.23
14	-	0.049	0.18	0.17
18/19	-	-	0.19	0.21
23	0.050	-	-	-
74/76	-	-	0.19	0.18
131/133	0.052	0.054	-	-

In a further study, samples of cherries were fortified with 0.1 or 1.0 mg/kg fenarimol and stored for 11 days in a chill room at 4°C, then for 93 days in the freezer at -20°C. Samples were analysed using the method of Griggs and Decker (1981). Recoveries were variable but acceptable. The results, corrected for procedural recoveries, were as shown in Table 19 (Day and Saunders, 1988b).

Table 19. Residues in cherries following storage at -20°C.

Fortification level, mg/kg	Residue, mg/kg			
	Sweet cherry		Sour cherry	
	0.1	1.0	0.1	1.0
Storage period (days)				
0	0.11, 0.11	1.1, 1.1	0.11, 0.11	1.1, 1.1
4	0.09, 0.11	1.1, 1.1	0.10, 0.11	1.1
7	0.12, 0.13	1.1, 1.10	0.13, 0.11	1.1, 1.2
11	0.12, 0.13	1.2, 1.3	0.15, 0.13	1.3, 1.3
30	0.10, 0.10	0.9, 1.0	0.11, 0.10	1.0, 1.0
68	0.10, 0.10	0.9	0.11, 0.10	0.93, 0.91
104	0.11, 0.11	1.1, 1.0	0.10, 0.10	1.2, 1.1

A new study on the stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditions was made available, but too late for review (Butcher, 1995g).

Residue definition

The animal and plant metabolism studies indicate that fenarimol is the major residue in products of both animal and plant origin. The residue is therefore defined as fenarimol.

USE PATTERN

Fenarimol is a systemic fungicide which has protective, curative and eradicative activity. Most commonly it is applied as a foliar treatment where apoplastic movement occurs through the leaf and towards the leaf tip, but movement from treated to untreated leaves is not sufficient to provide disease control. Application via the roots and seeds leads to translocation to all the aerial parts of the plant.

Fenarimol is registered in a large number of countries. Its uses cover a wide range of fruit and vegetables, hops and wheat. Full details of registered use patterns are given in Tables 20-22. The registered uses are for treatments in the field unless otherwise indicated.

Table 20. Registered uses of fenarimol on fruits and pecans.

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Apples	Australia	EC	airblast	0.043-0.054	0.0029-0.0036	1-10	14	1 & 2
	Argentina	EC	mist blower broadcast	0.048-0.09	0.0024-0.003	2	20	1

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Belgium	WP	LV overall	0.03-0.06	-------	3-4	1 month	1
	Brazil	EC	mist blower broadcast	0.038-0.14	0.0048-0.0072	2	28	1
	Chile	EC	Gun broadcast med vol	0.038-0.096	0.0036-0.0042	2	(a)	1
	Denmark	EC	HV overall	0.060	0.006-0.004	5	14	1 & 11
	Germany (Rubigan EC)	EC	L/HV row	0.0108-0.054	0.0036	max 7	21	1 & 8
	Germany (Elital)	SC	L/HV overall	0.0108-0.054	0.0036	max 14	21	1 & 8
	Germany (Rubigan SC)	SC	L/HV row	0.0108-0.054	0.0036	max 14	21	1 & 8
	Greece	WP	HV overall	0.105	0.0042	3-5	20	1
	Ireland	SC	LV overall	0.04-0.08	-------	up to 14 usually 4-6	14	1
	Italy	EC	HV overall	0.054-0.072	0.0036-0.0048	Through-out season	21	1
	Italy	SC	HV overall	0.054-0.072	0.0036-0.0048	Through-out season	21	1
	Italy	WP	HV overall	0.054-0.072	0.0036-0.0048	Through-out season	21	1
	Japan	WP	airblast	0.09-~0.14	0.003-~0.004	1-3	21	1
	Mexico	EC	mist blower	0.054-0.108	0.0027-0.0036	2	(b)	1
	Netherlands[1] (country submission)	WP	spraying of the aerial part	0.039-0.076	0.0039-0.076	3	21	6
	Netherlands (company submission)	WP	HV overall	0.039-0.076	0.0026-0.076	max 10	3 weeks	1
	New Zealand	SC	HV to run-off	0.0067-0.090	0.003	6	35	5
	Peru[1] (country submission)	-	foliar application	-	0.05	3	30	7
	Peru (company submission)	EC	gun broadcast	0.012-0.060	0.0015-0.004	2	(a)	1
	Portugal	EC	HV overall	0.024-0.054	0.0024-0.0036	5	21	1
	Spain	EC	low volume spray (500-1,500 l/ha)	-	0.0042-0.0048	7-10 days intervals	14	4
	Spain	EC	high volume spray (>1,500 l/ha)	0.060-0.096	-	7-10 days intervals	14	4
	Spain	SC	HV overall	0.063-0.072	0.0042-0.0048	1	14	1
	UK	SC	LV overall	0.04-0.08	-------	up to 14 usually 4-6	14	1
	Uruguay	EC	broadcast mist blower	0.075-0.090	0.0024-0.003	2	20	1
	USA	SC	spray	0.049-0.098	-	7-14***	30	4
	USA	EC	spray	0.067-0.101	-	7-10***	30	4

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Bananas	Honduras[1]	EC	Aerial	0.08-0.12	0.0053-0.006	7	0 (c)	1
	Nicaragua[1]	EC	Aerial	0.08-0.12	0.533-0.6	7	0 (c)	1
Currants								
, black	Denmark	EC	HV overall	0.06	--------	3	14	1
, black	Ireland	SC	LV overall	0.04	--------	NR	14	1
	Netherlands[1] (country submission)	EC	spray	0.048-0.058	0.0048	4	21	6
	Netherlands (company submission)	EC	HV overall	0.048-0.058	0.0048	5	3 weeks	1
, black	UK	SC	LV overall	0.04	--------	NR	14	1
Cherry	Denmark	EC	HV overall	0.060	--------	5	14	1
	Japan	WP	airblast	0.16 ~0.2	0.004	1-3	3	1
	USA	EC	spray	0.051-0.101	-	4-8***	up to & after harvest	4
Gooseberries	Ireland	SC	HV overall	0.04	-------	NR	14	1
	Netherlands	EC	spray	0.048-0.058	0.0048	4	21	1
	UK	SC	HV overall	0.04	-------	NR	14	1
Grapes	Argentina	EC	gun individual plant	0.0192-0.036	0.0024	2	30	1
	Australia	EC	airblast	0.012-0.024	0.0012-0.0024	1-7	14	1
	Brazil	EC	gun individual plant	0.0108-0.024	0.0018-0.0024	4	15	1
, table	Chile	EC	gun individual plant	0.005 0.012	0.002-0.003	3	(d)	1
	France	SC	LV overall	0.018	0.0009-0.003	1 to 4	7	1
, wine	Germany[1] (Elital) (country submission)	SC	spray	0.0047-0.0125	0.00078	6	35	8
	Germany (Elital) (company submission)	SC	L/HV overall	0.0047-0.0234	0.00156	max 6*	35	1
	Germany (Rubigan SC)	SC	L/HV row	0.0047-0.0234	0.00156	max 6	35	1
	Greece	WP	HV overall	0.012-0.024	0.0012-0.0024	2-4	30	1
	Ireland	SC	LV overall	0.04	-------	NR	14	1
,table	Italy	WP	HV overall	0.03-0.06			14	1
,table	Italy	SC	HV overall	0.018-0.036	0.0018-0.0036	--------	14	1
, wine	Italy	SC	HV overall	0.014-0.054	0.0018-0.0036	--------	14	1
, wine	Italy	WP	HV overall	0.014-0.036	0.0018-0.0036		14	1
	Mexico	EC	mist blower	0.030-0.054	0.0075-0.0054	4	(e)	1
	New Zealand	SC	HV spray to run-off	0.024-0.048	0.0024	4	30	5
	Peru[1] (country	-	foliar	-	0.02	4	30	7

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	submission)		application					
	Peru (company submission)	EC	gun broadcast	0.012-0.060	0.0012-0.005	3	(d)	1
	Portugal	EC	HV overall	0.011-0.03	0.0018-0.0030	3	7	1
	Spain	EC	MV-HV overall	0.0099-0.05	0.0033-0.0036	1 (wine) 3(table)	28 (wine) 14 (table)	1
	Spain	SC	MV-HV overall	0.009-0.05	0.003-0.0036	1 (wine) 3(table)	28 (wine) 14 (table)	1
	UK	SC	spray	0.04	-------	NR	14	1 & 4
	Uruguay	EC	gun application individual plant	0.019-0.036	0.0024	2	30	1
	USA	EC	spray	0.017-0.051	_	3-9***	30	4
	USA	SC	spray	0.024-0.049	-	2-7***	30	4
Peaches	Argentina	EC	mist blower	0.048-0.072	0.0024	2	20	1
	Greece	WP	HV overall	0.12	0.0048	2-4	20	1
	Italy	EC	HV overall	0.072	0.0042-0.0048	2-3	14	1 & 12
	Italy	SC	HV overall	0.072	0.0042-0.0048	2-3	14	1 & 12
	Japan	WP	airblast	0.12-~0.2	0.004	1-3	1	1
	Spain	EC	HV overall	-	0.0042-0.0048	1	7	4
	Spain	SC	HV overall	-	0.0042-0.0048	1	7	4
	Uruguay	EC	broadcast mist blower	0.048-0.072	0.0024	2	20	1
Pears	Argentina	EC	mist blower broadcast	0.048-0.09	0.0024-0.003	2	20	1
	Australia	EC	airblast	0.043-0.054	0.029-0.0036	1-10	14	1 & 2
, Japanese	Australia	EC	airblast	0.036-0.054	0.0024-0.0036	1-10	14	1 & 2
	Belgium	WP	LV overall	0.03-0.06	--------	3-4	1 month	1
	Chile	EC	Gun broadcast med. vol	0.038-0.096	0.0036 0.0042	2	(a)	1
	Denmark	EC	HV overall	0.060	--------	5	14	1
	Germany (Elital)	SC	L/HV overall	0.0108-0.054	0.0036	max 14	21	1 & 8
	Italy	EC	HV overall	--------	0.0036-0.0048	**	14	1
	Italy	SC	HV overall	--------	0.0036-0.0048	**	14	1
	Italy	WP	HV overall	0.054-0.072	0.0036-0.0048	**	14	1

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Japan	WP	airblast	0.09-~0.12	0.003-~0.004	1-3	21	1
	Mexico	EC	mist blower	0.054-0.108	0.0027-0.0036	2	(b)	1
	Netherlands[1] (country submission)	WP	spraying of the aerial part	0.039-0.076	0.0039-0.076	3	21	6
	Netherlands (company submission)	WP	HV overall	0.039-0.076	0.0026-0.0076	max 10	3 weeks	1
	New Zealand	SC	HV to run-off	0.0067-0.090	0.003	6	35	5
	Portugal	EC	HV overall	0.024-0.054	0.0024-0.0036	5	21	1
	Spain	EC	HV overall	0.063-0.072	0.0042-0.0048	1	14	1
	Spain	SC	HV overall	0.063-0.072	0.0042-0.0048	1	14	1
	Uruguay	EC	broadcast mist blower	0.075-0.090	0.0024-0.003	2	20	1
	USA	SC	spray	0.049-0.098	-	7-14***	30	4
	USA	EC	spray	0.067-0.101	-	7-10***	30	4
Pecans	Mexico	EC	mist blower	0.054-0.108	0.0028-0.0057	2	(f)	1
	USA	SC	applied to run-off	0.073-0.098	-	7-9***	30	4
Persimmon, Japanese	Japan	WP	airblast	0.2	0.004	1-3	21	1
Raspberry	UK	SC	LV overall	0.04	--------	3	14	1
	Ireland	SC	LV overall	0.04	--------	3	14	1
Strawberry	Denmark	EC	HV overall	0.084	--------	3	14	1
	Ireland	SC	LV overall	0.04	--------	NR	14	1
	Italy	EC	HV overall	--------	0.0042-0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0042-0.0048	3	7	1
	Italy	WP	HV overall	0.034-0.038	0.0042-0.0048	3	7	1
	Japan	WP	mist spray[2]	0.03	0.003	1-3	1	1 & 10
	Netherlands[1] (country submission)	EC	spray[2]	0.036-0.084 (depend. on variety)	0.006-0.0084	4	treatment before flowering or after harvest	6
	Netherlands (company submission)	EC	HV overall	0.03-0.05	0.005-0.01	5	treatment before flowering or after harvest	1
	Spain	EC	HV overall		0.0042-0.0048	4	3	1
	Spain	SC	HV overall		0.0036-0.0048	4	3	1

Commodity	Country	Form	Application				PHI, days	Ref.
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	UK	SC	LV overall	0.04	-------	NR	14	1

[1] No product label submitted
[2] Glasshouse and Field use
NR No restration restriction, typically 2-4
* max 4 between flowering and benning of ripening
** Application throughout season
*** the maximum number of treatments is controlled by a maximum total dose
Notes (a) to (f) refer to growth stage at last treatment:
(a) immature fruit (b) early fruit
(c) from disease onset (d) mature fruit
(e) fruit initiation (f) pre-flowering

Table 21. Registered uses of fenarimol on vegetables.

Crop	Country	Form	Application				PHI, days	Refer-ence
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
Artichokes	Italy	EC	HV overall	--------	0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
Aubergines	Italy	EC	HV overall	--------	0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Japan	WP	mist spray	0.024 ~0.04	0.0012 ~0.002	1-3	1	1
Courgettes	Netherlands[1] (country submission)	EC	spray[2]	0.012-0.036	0.0024	6	3	6
	Netherlands[1] (country submission)	EC	spray (field only)	0.0096-0.024	0.0024	6	3	6
Cucumbers	Brazil	EC	knapsack individ. plant	0.038-0.072	0.0048-0.0072	4	4	1
	Denmark	EC	HV overall[3]	0.024-0.036	0.0024	4-8	2	1
	Ireland	SC	LV overall	--------	0.001-0.002	NR	2	1
	Japan	WP	mist spray	0.024	0.0012	1-3	1	1
	Netherlands	EC	spray[2]	0.012-0.036	0.0024	6	3	1
	UK	SC	LV overall[3]	--------	0.001-0.002	NR	2	1
	Uruguay	EC	knapsack individ. plant	0.014-0.024	0.0012-0.0024	4	4	1
Cucurbits	Australia	EC	Boom	0.024	0.004	1-10	3	1
	Greece	WP	HV overall	0.018-0.024	0.0018-0.0024	as requir ed	1	1
	Italy	EC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	SC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	WP	HV overall	0.020-	0.0024-	3	7	1

Crop	Country	Form	Application				PHI, days	Reference
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
				0.024	0.003			
	Spain	EC	HV overall	0.01-0.019	0.0036-0.0048	2	7	1
	Spain	SC	HV overall	0.013-0.019	0.0042-0.0048	2	7	1
Egg plants, see Aubergines								
Gherkins	Netherlands[1] (country submission)	EC	spray[2]	0.012-0.036	0.0024	6	3	6
	Netherlands[1] (country submission)	EC	spray (field only)	0.0096-0.024	0.0024	6	3	6
Melons	Japan	WP	mist spray	0.024	0.0012	1-4	1	1
	Netherlands	EC	spray[2]	0.012-0.036	0.0024	6	3	1
	Portugal	EC	HV overall	0.024-0.036	0.0024-0.0036	5	3	1
Musk-melons	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
Peas	Italy	EC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	SC	HV overall	--------	0.0024-0.003	3	7	1
	Italy	WP	HV overall	0.02-0.024	0.0024-0.003	3	7	1
Peas, Immature	Japan	WP	mist spray	0.024	0.0012	1-5	1	1
Peppers	Italy	EC	HV overall	--------	0.0048	3	7	1
	Italy	SC	HV overall	--------	0.0048	3	7	1
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Netherlands[1] (country submission)	EC	spray[2]	0.012-0.036	0.0024	6	3	6
	Japan	WP	mist spray	0.024	0.0012	1-4	1	1
	Spain	EC	HV overall	0.048-0.072	0.0048-0.006	3	7	1
	Spain	SC	HV overall	0.048-0.072	0.0048-0.006	3	7	1
	UK	SC	overall spray[2]	0.054	0.002	3	7	9
Pumpkins	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
	Japan	WP	mist spray	0.012	0.0012	1-4	3	1
	Peru	EC	gun individ. plant	0.012-0.060	0.0015-0.004	4	4	1
Squash, small	Argentina	EC	gun individ. plant	0.0096-0.024	0.0012-0.0024	4	4	1
Squash	Uruguay	EC	knapsack individ. plant	0.014-0.024	0.0012-0.0024	4	4	1
Squash, summer	Netherlands	EC	spray[2]	0.012-0.036	0.0024	6	3	1
Tomatoes	Denmark	EC	HV overall[3]	0.024-0.036	0.0024	4-8	2	1
	Italy	EC	HV overall	---------	0.0048	3	7	1
	Italy	SC	HV overall	---------	0.0048	3	7	1

Crop	Country	Form	Application				PHI, days	Refer-ence
			Method	Rate kg ai/ha	Spray conc, kg ai/hl	No.		
	Italy	WP	HV overall	0.038	0.0048	3	7	1
	Japan	WP	mist spray	0.04	0.002	1-3	1	1
	Netherlands[1] (country submission)	EC	spray[2]	0.024-0.072	0.0048	3	3	6
	Netherlands (company submission)	EC	HV overall	0.024-0.072	0.0048	5	3	1
	Spain	EC	HV overall	0.028-0.057	0.0048	3	7	1
	Spain	SC	HV overall	0.028-0.057	0.0048	3	7	1
	UK	SC	overall spray[2]	0.054	0.002	3	7	9
Watermelons	Brazil	EC	knapsack individ. plant	0.014-0.024	0.0018-0.0024	4	4	1
	Japan	WP	mist spray	0.012	0.0012	1-4	3	1
	Uruguay	EC	knapsack individ. plant	0.0096-0.0024	0.0012-0.0024	4	4	1
Vegetables	Netherlands	EC	HV overall	0.012-0.036	0.0024	5	3	1

[1] No product label submitted
[2] Glasshouse use only
[3] Glasshouse and field use

Table 22. Registered uses of fenarimol on hops and cereals.

Crop	Country	Form	Application				PHI, days	Ref.
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.		
Hops	Germany	WP	HV row	0.06	0.0015	max 4	10	1 & 8
	Spain	EC	HV overall		0.0042-0.0048		--------	1
	Spain	SC	HV overall		0.0042-0.0048		--------	1
Wheat	Japan	WP	Boom	0.04-0.06	0.004	1-2	14	1

Uses of fenarimol were also reported in Algeria, Austria, "Belarus", Bulgaria, China, "CR/SR", Croatia, Egypt, Hungary, India, Indonesia, Iraq, Korea, Lebanon, Libya, Macedonia, Morocco, Pakistan, Poland, Romania, Russia, Slovenia, Slovakia, Switzerland, Syria, Taiwan and Tunisia, but insufficient information was submitted for inclusion in the Tables.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The residue trials are summarized in the following Tables. Trials were carried out under field conditions unless stated otherwise. Unless indicated in the notes, trials were reported in sufficient detail and acceptable analytical information was supplied. Analytical recoveries outside the range 70-120% and/or storage of samples for longer than 6 months are also indicated in the notes. Analytical results have been rounded to one significant figure if <0.1 mg/kg except where processing information is given.

Apples. Informatiaon on GAP was reported for many countries world-wide. The maximum

application rates are 0.054-0.14 kg ai/ha with PHIs of 14-35 days.

Residue trials data were available from Belgium, Germany, the UK, Canada, the USA, Chile, Brazil, New Zealand and The Netherlands. Residues in 16 Northern European trials according to German GAP (0.0036 kg ai/hl, 21-day PHI) were 0.02-0.21 mg/kg. Three further trials which reflected German GAP showed residues of 0.06, 0.1 and 0.1 mg/kg but only a summary was submitted. Eight Northern European trials complied with GAP in Denmark, the UK and Ireland in which there is a shorter PHI of 14 days (maximum rates 0.06-0.08 kg ai/ha, concentration not specified) with residue levels of 0.02-0.18 mg/kg. A further 6 Dutch trials were within GAP in The Netherlands (0.0039-0.076kg ai/hl, 21-day PHI) with residues of 0.01-0.34 mg/kg in samples taken 21 days after the final treatment. However, these Dutch trials were submitted in summary form only. In 5 replicated US trials according to GAP (ca 0.1 kg ai/ha, 30-day PHI) residue levels were 0.002-0.3 mg/kg. In three New Zealand trials according to GAP (maximum 0.09 kg ai/ha, 0.003 kg ai/hl, 35-day PHI) residues were 0.008-0.03 mg/kg.

Table 23. European supervised residue trials on apples.

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Ramecroix, Belgium, 1976[1]	EC	11	0.034	0.004	0	0.12	NF 13 B76-001
					7	0.07	
					14	0.05	
					21	0.06	
					28	0.04	
					85	0.01	
Giessen, Germany, 1977[1]	EC	10	0.036	0.003	55	<0.01	NF 15 D76-302
			0.048	0.004	55	<0.01	
Giessen, Germany, 1978[2,3,5]	EC	14	0.054	0.0036	0	0.13	NF 08 D78-311
					3	0.12	
					7	0.10	
					10	0.11	
					14	0.07	
					21	0.06	
					28	0.08	
					36	0.07	
Giessen, Germany, 1981[3,5]	SC	14	0.054	0.0036	0	0.16	NF 20 D81-302
					4	0.06	
					13	0.05	
					20	0.07	
					27	0.04	
					33	0.06	
Uberlingen, Germany, 1981[3,4,5]	SC	14	0.054	0.0036	0	0.29	NF 20 D81-353
					4	0.34	
					7	0.02	
					14	0.02	
					21	0.02	
Wulfsdorf, Germany, 1981[3,5]	SC	13	0.054	0.0036	0	0.36	NF 20 D81-350
					7	0.23	
					14	0.18	
					22	0.06	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					28	0.05	
					35	0.05	
Wittlich, Germany, 1981[3,4,5]	SC	10	0.06	0.00396	0	0.37	NF 20 D81-351
					7	0.19	
					14	0.15	
					21	0.15	
					28	0.09	
					63	0.01	
Kriftel, Germany, 1982[3,5]	EC	13	0.036	0.0036	0	0.06	NF 21 D82-304
					8	0.05	
					14	0.04	
					17	0.04	
	SC	13	0.036	0.0036	0	0.1	
					8	0.09	
					14	0.07	
					17	0.04	
Kriftel, Germany, 1982[3,5,6]	EC	13	0.036	0.0036	0	0.09	NF 21 D82-305
					8	0.08	
					14	0.06	
					21	0.05	
					30	0.03	
	SC	13	0.036	0.0036	0	0.21	
					8	0.17	
					14	0.04	
					21	0.11	
					30	0.05	
Marbach, Germany, 1982[3,5]	EC	14	0.036	0.0036	0	0.37	NF 21
					7	0.24	
					13	0.22	
					20	0.21	
					27	0.14	
Marbach, Germany, 1982[3,5]	EC	14	0.036	0.0036	0	0.18	NF 21 D82-307
					7	0.11	
					13	0.15	
					20	0.14	
					27	0.09	
Giessen, Germany, 1982[3,5,6]	EC	14	0.036	0.0036	0	0.17	NF 21 D82-301
					5	0.08	
					13	0.05	
					19	0.03	
					26	0.04	
					35	0.01	
	SC	14	0.036	0.0036	0	0.19	
					5	0.11	
					13	0.08	
					19	0.07	
					26	0.04	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					35	0.02	
Giessen, Germany, 1982[3,5]	SC	14	0.036	0.0036	0	0.10	NF 21 D82-302
					5	0.12	
					13	0.06	
					19	0.04	
					26	0.04	
					35	0.03	
	EC	14	0.036	0.0036	0	0.10	
					5	0.07	
					13	0.03	
					19	0.03	
					26	0.01	
					35	0.02	
Giessen, Germany, 1982[3,5,6]	EC	14	0.036	0.0036	0	0.06	NF 21 D82-303
					8	0.03	
					14	0.03	
					21	0.02	
					30	0.01	
	SC	14	0.036	0.0036	0	0.10	
					8	0.09	
					14	0.01	
					21	0.03	
					30	0.01	
Bonn, Germany, 1982[1]	EC	12	0.05	0.004	0	0.1	8
					7	0.1	
					14	0.1	
					21	0.1	
					28	0.04	
Dossenheim, Germany, 1982[1]	EC	14	0.05	0.004	0	0.1	8
					10	0.1	
					14	0.04	
Frankfurt, Germany, 1982[1]	EC	14	0.05	0.004	0	0.1	8
					10	0.1	
					14	0.1	
					21	0.1	
					28	0.02	
Oudenbosch, Netherlands, 1977[5,7]	WP	1		0.005	7	0.14	6
						0.14	
						0.22	
						0.17	
					14	0.1	
						0.14	
						0.15	
						0.09	
					21	0.09*	
						0.01*	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
						0.11*	
						0.06*	
Berlicum, Netherlands, 1977[5,7]	WP	1		0.005	7	0.33	6
						0.41	
						0.3	
						0.37	
					14	0.21	
						0.46	
						0.35	
						0.24	
					21	0.28*	
						0.21*	
						0.26*	
						0.34*	
Breskens, Netherlands, 1977[5,7]	WP	1		0.005	7	0.27	6
						0.34	
						0.22	
						0.19	
					14	0.16	
						0.12	
						0.13	
						0.15	
					21	0.22*	
						0.22*	
						0.18*	
						0.14*	
Knuiningen, Netherlands, 1978[5,7]	WP	1		0.005	8	0.09	6
					15	0.11	
					22	0.06*	
Knuiningen, Netherlands, 1978[5,7]	WP	1		0.005	9	0.09	6
					15	0.06	
					22	0.03*	
Knuiningen, Netherlands, 1978[5,7]	WP	1		0.005	7	0.14	6
					14	0.11	
					21	0.13*	
Surrey, UK, 1981[3,5]	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.17	NF 20 FF81-002-01
					7	0.12	
					14	0.04	
					21	0.07	
Surrey, UK, 1981[3,5]	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.30	NF 20 FF81-002-02
					7	0.18	
					14	0.10	
					21	0.09	

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Surrey, UK, 1981[3,5]	SC	13	0.06	0.003 x 11 0.002 x 2	0	0.31	NF 20 FF81-002-03
					7	0.19	
					14	0.14	
					21	0.13	

Underlined residues are from treatments according to GAP in Germany; those underlined twice from treatments according to GAP in Denmark, Ireland and the UK.
* According to GAP in The Netherlands.
[1] No detailed report submitted
[2] No weather data submitted
[3] Method of analysis unspecified
[4] Crops stored for 7 (NF20 D81-351) or 8 months (NF20 D81-353) before analysis
[5] No example chromatograms submitted
[6] High associated recoveries (NF21: D82-305 113-126%; D82-301 102-126%; D82-303 110-127%)
[7] Report not in English

Table 24. Non-European supervised residue trials on apples (including US processing trials).

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Ontario, Canada, 1975[1,2,7]	EC	13	0.025	0.002	42	fruit	0.01	NF 25 MFM 5-1
			0.05	0.004		fruit	0.02	
			0.075	0.008		fruit	0.04	
Ontario, Canada, 1975[1,2,7]	EC	13	0.025	0.002	42	fruit	0.02	NF 25 MFM 6-1
			0.03	0.004		fruit	0.02	
			0.05	0.004		fruit	0.02	
			0.075	0.008		fruit	0.06	
Ontario, Canada, 1976[1,2,7]	EC	12	0.097	0.002	34	fruit	0.01	NF 25 MFM 6-3
			0.134	0.004		fruit	0.02	
			0.270	0.004		fruit	0.06	
		11	0.16 x 4 0.08 x 7	0.004 x 4 0.002 x 7		fruit	0.04	
Meaford, ONT, Canada, 1977 [1,2,7,9]	EC	6	0.016			fruit	0.007	NF 26 MFM 7-12
		6			15	fruit	0.05	
Bowmanville, ONT, Canada, 1977[1,2,7,9]	EC	5	0.016			fruit	0.17	NF 26 MFM 7-14
London, ONT, Canada, 1977[1,2,7,9]	EC	8	0.012		28	fruit	0.02	NF 26 MFM 7-28
Simcoe, ONT, Canada, 1977[1,2,7,9]	EC	8	0.012		84	fruit	0.03	NF 26 MFM 7-29
Simcoe, ONT, Canada, 1977[1,2,7,9]	EC	10	0.016 x 8 0.08 x 2			fruit	0.03	NF 26 MFM 7-31
		10	8 x 0.141 or 0.016 2 x 0.069 or			fruit	0.03	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
			0.08					
Nattawa, ONT, Canada, 1977[1,2,7,9]	EC	6	0.016		83	fruit	0.007	NF 26 MFM 7-34
		6	0.016		83	fruit	0.003	
Meaford, ONT, Canada, 1977[1,7]	EC	6	0.142		15	fruit	0.07	NF 27 MFM 7-12
		6	0.142			fruit	0.05	
Bowmanville, ONT, Canada, 1977[1,7]	EC	5	0.142		69	fruit	0.02	NF 27 MFM 7-14
London, ONT, Canada, 1977[1,7]	EC	8	0.1		28	fruit	0.02	NF 27 MFM 7-38
Simcoe, ONT, Canada, 1977[1,7]	EC	8	0.1		86	fruit	0.03	NF 27 MFM 7-29
Simcoe, ONT, Canada, 1977[1,7]	EC	8	6 x 0.142 2 x 0.071		45	fruit	0.03	NF 27 MFM 7-33
Simcoe, ONT, Canada, 1977[1,7]	EC	6	0.142		90	fruit	0.003	NF 27 MFM 7-34
Nottawa, ONT, Canada, 1977[1,7]	EC	6	0.142		90	fruit	0.007	NF 27 MFM 7-34
Oyamba, BC, Canada, 1980[1,7]	EC	3	0.101		131	fruit	0.003	NF 27 K Ellison
					95	fruit	0.004	
Kelowna, BC, Canada, 1980[1,7]	EC	3	0.101		121	fruit	<0.002	NF 27 E. Star
West Bank, BC, Canada, 1980[1,7]	EC	3	0.101		121	fruit	0.03 <0.002	NF 27 M. Janse
Campinas, Brazil, 1985[1,6,7]	EC	9		0.018	28	fruit	0.01	NB 29
				0.036		fruit	0.04	
Curico, Chile, 1980[1,3,7,12]	EC	9	0.06		100	fruit	0.09 0.09	NF 28
	SC					fruit	0.06	
San Fernando, Chile, 1980[1,3,7,12]	EC	6	0.06		113	fruit	0.08	
			0.048			fruit	0.003	
Albany, NZ, 1976[1]	EC	10	0.132	0.002-0.004	2	fruit	0.07	NF 29 NZ 75-19
					6	fruit	0.05	
					12	fruit	0.04	
			0.099	0.0015-0.003	2	fruit	0.07	
					6	fruit	0.05	
					7	fruit	0.07	
					21	fruit	0.06	
					35	fruit	0.02	
Hastings, NZ, 1979[1]	WP	12	0.061	0.0025	52	fruit	0.008	NF 29 NZ 78-2
			0.061	0.003		fruit	0.006	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Hamilton, NZ, 1980[1]	WP	1	0.048		120	fruit	<0.002	NF 29 NZ 80-6
Hamilton, NZ, 1980[1]	WP	8	0.081		1	fruit	0.02	NF 29 NZ 80-5
					8	fruit	0.02	
					15	fruit	0.01	
					29	fruit	0.008	
Christchurch, NZ, 1981[1]	WP	14		0.003	31	fruit	0.03	NF 29 T Holland
					38	fruit	0.03	
					45	fruit	0.01	
Geneva, NY, USA, 1981[1,2,4]	EC	6	0.0445		107	fruit	<0.002	NF 18 Cornel
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.003	
						dry pomace	0.025	
		3 3	0.0445 0.0223		107	fruit	0.002	
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.002	
						dry pomace	0.014	
Biglerville, PA, USA, 1981[1,2,4,9]	EC	11	0.1038		42	fruit	0.037	NF 18 Penn. Univ.
						juice	0.003	
						sauce	0.009	
						wet pomace from sauce	0.20	
						dry pomace	0.67	
		4 7	0.1038 0.0519		42	fruit	0.017	
						juice	<0.002	
						sauce	0.004	
						wet pomace from sauce	0.079	
						dry pomace	0.20	
Winchester, VA, USA, 1981[1,2,4,9]	EC	10	0.1038		34	fruit	0.059	NF 18 Winchester
						juice	0.002	
						sauce	0.015	
						wet pomace from sauce	0.14	
						dry pomace	0.31	
		3 7	0.1038 0.0519			fruit	0.057	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						juice	0.002	
						sauce	0.01	
						wet pomace from sauce	0.015	
						dry pomace	0.36	
Sodus, NY, USA, 1982[1,2,3,4,9,12]	EC	1 10	0.316 0.105		41	juice	0.002	NF 18 CMR 82-9
						wet pomace from juice	0.049	
						sauce	<0.002	
						dry pomace	0.11	
		1 10	0.316 0.105		41	juice	<0.002	
						wet pomace from juice	0.061	
						sauce	<0.002	
						dry pomace	0.13	
Sodus, NY, USA,1982[1,2]	EC	8	0.105		63	fruit	0.014	NF 18 CMR 8-10
						juice	0.002	
						wet pomace from juice	0.073	
						sauce	<0.002	
						dry pomace	0.12	
		8	0.105		63	fruit	0.008	
						juice	0.002	
						wet pomace from juice	0.072	
						sauce	<0.002	
						dry pomace	0.16	
Sodus, NY, USA, 1982[1,2]	EC	8	0.079		83	fruit	<0.002	NF 18 CMR 82-11
						juice	<0.002	
						wet pomace from juice	0.006	
						sauce	<0.002	
						dry pomace	0.012	
		8	0.079		83	fruit	<0.002	
						juice	0.002	
						wet pomace from juice	0.003	
						sauce	<0.002	
						dry pomace	0.013	
Sodus, NY, USA, 1982[1,2]	EC	10	0.0789		53	fruit	0.007	NF 18 CMR 82-16
						juice	<0.002	
						sauce	<0.002	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						wet pomace from sauce	0.068	
						dry pomace	0.12	
		10	0.0789		53	fruit	0.007	
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	0.079	
						dry pomace	0.098	
Daleville, VA, USA, 1982[1,2,4]	EC	8	0.1052		33	fruit	0.002	NF 18 DAA 82-6
						juice	<0.002	
						wet pomace from juice	0.013	
		11	0.1052		33	fruit	0.002	
						juice	<0.002	
						wet pomace from juice	0.009	
Tehachapi, CA, USA, 1982[1,2,9]	EC	4	0.2105		118	fruit	<0.002	NF 18 DHF 82-12
						juice	<0.002	
						wet pomace from juice	0.009	
Gardners, PA, USA, 1982[1,2,11]	EC	8	0.0526		136	fruit	<0.002	NF 18 PEB 82-5
						juice	<0.002	
						sauce	<0.002	
						wet pomace from sauce	<0.002	
Thurmont, MD, USA, 1982[1,2]		10	0.1052		70	fruit	0.02	NF 18 PEB 82-6
						juice	0.002	
						sauce	0.003	
						wet pomace from sauce	0.036	
Gettysburgh, PA, USA, 1982[1,2,11]		10	0.0526		75	fruit	0.021	NF 18 PEB 82-14
						juice	0.003	
						sauce	<0.002	
						wet pomace from sauce	0.054	
Watsonville, CA, USA,1982[1,2,9]		4	0.1052		104	fruit	0.005	NF 18 RAH 82-1
						juice	0.002	
						wet pomace from juice	0.018	
		4	0.2105		104	fruit	0.013	
						juice	0.003	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
						wet pomace from juice	0.043	
Snelling, CA, USA, 1982[1,2,9]		4	0.1052		93	fruit	0.008	NF 18 RAH 82-2
						juice	0.002	
						wet pomace from juice	0.021	
		4	0.2105		93	fruit	0.011	
						juice	0.002	
						wet pomace from juice	0.029	
Moxee, WA, USA, 1982[1,2]		1 3	0.084 0.104		122	fruit	0.002	NF 18 WTC 82-4
						juice	<0.002	
						wet pomace from juice	0.005	
		1 3	0.104 0.132		122	fruit	0.002	
						juice	<0.002	
						wet pomace from juice	0.004	
Orondo, WA, USA, 1982[1,2]		2 2	0.105 0.132		147	fruit	0.007	NF 18 WTC 82-8
						juice	<0.002	
						wet pomace from juice	0.015	
Covert, MI, USA, 1982[1,2,9]		10	0.1052		147	fruit	0.019	NF 18 DG 082-10
						juice	<0.002	
						wet pomace from juice	0.14	
						sauce	0.003	
						wet pomace from sauce	0.33	
Sodus, NY, USA, 1976[1,2]		10	0.1075		62	fruit	0.004	NF 18 CDC 6-16
						juice	<0.002	
						wet pomace from juice	0.022	
						dry pomace	0.068	
Reedley, CA, USA, 1988	EC	7	0.105		30	fruit	0.03	NF 31 DHF88-02
		7	0.105		30	fruit	0.02	NF 31 DHF 88-03
Sunnyside, WA, USA, 1988	EC	7	0.105		29	fruit	0.01	NF 31 BJB88-01
		7	0.105		29	fruit	0.01	NF 31 BJB88-02
		7	0.105		29	fruit	0.02	NF 31

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
								BJB88-03

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in New Zealand
[1] No weather data submitted
[2] Method of analysis unspecified. Stated to be GLC for studies NF 20, 25 & 26 but no further details
[3] No control plot data submitted
[4] Crops stored for 8-15 months before analysis
[6] No example chromatograms submitted
[7] Duration of sample storage unspecified
[9] High associated recoveries (NF26: MFM 7-12 98-140%, NF 18 dry pomace 132%; juice 121-128%
[11] Half sprayed - one side of row only
[12] System recoveries only submitted (i.e control extract or extraction solvent, not the commodity, was fortified)

Pears. GAP was reported for many countries world-wide and was generally the same as that reported for apples.

A few trials were available which complied with GAP (the same as for apples) in Germany (one trial), Italy (one trial) or the USA (4 trials with replicates), but the recoveries associated with the German (0.13 mg/kg) and Italian trials (0.09 mg/kg) were low at 67 and 63% respectively. Residues in the US trials were 0.01-0.04 mg/kg.

Table 25. Supervised residue trials on pears.

Location, year	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
Australia, 1985[1,5,6]				0.0036	14	0.03	NB 30 AUS 78-314
				0.0072		0.04	
Giessen, Germany, 1978[1-4,6]	EC	14	0.054		0	0.1	NF 03 D78-312
					3	0.08	
					10	0.07	
					13	0.08	
					17	0.08	
					20	0.09*	
					24	0.03	
					31	0.06	
Baricella, Italy, 1981[1-4]	SC	17		0.004	20	0.13	NF 06 181 211
Hood River, OR, USA, 1983[1,5]	EC	3	0.143		112	0.003	NF 33 WTC83-2
Medford, OR, USA, 1983[1,5]	EC	2	0.143		120	<0.001	NF 33 830R12
					144	<0.001	
Hood River, OR, USA, 1984[1,5]	EC	3	0.092		120	<0.001	NF 33 840R4
			0.143		123	<0.001	
Medford, OR, USA, 1985[1,5]	EC	2	0.092 0.071		147	<0.001	NF 33 840R5
			0.143 0.109			<0.001	
Clayton, NC, USA, 1986[1,5]	SC	7	0.1		30	0.01	NF 33 DAA86-13
		7	0.1			0.02	
Reedley, CA, USA, 1986	SC	7	0.1		30	0.03	NF 33 DHF86-5

Location, year	Application				PHI, days	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl			
	EC					0.01	
Parlier, CA, USA, 1986[1,5]	EC	7	0.1		29	0.04	NF 33 DHF86-6
Mesa, WA, USA, 1986[1,5]	EC	7	0.1		28	0.02	NF 33 DHF86-8
	SC					0.08	

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in Italy
* according to GAP in Germany
[1] No weather data submitted
[2] Method of analysis unspecified
[3] Low associated recoveries (NF03 D78-312 67%; NF06 181-211 63%
[4] No example chromatograms submitted
[5] Duration of sample storage unspecified
[6] Crop variety unspecified

Peaches. GAP was reported for Uruguay, Argentina, Japan, Greece, Italy and Spain. No GAP was reported for apricots or nectarines, although some trials data were submitted. The maximum application rates are 0.036-0.2 kg ai/ha (0.0024-0.0048 kg ai/hl) with a PHI of 1-20 days.

Residue trials were available only from Spain, Italy and France. The critical European GAP for peaches was the Spanish (0.0048 kg ai/hl, PHI 7 days) for which there were 5 trials (one of them replicated) with residues of 0.03-0.3 mg/kg. In two of these trials the volume of spray per hectare was not specified. A further Spanish trial on apricots in 1988 where the use pattern was the same as the Spanish GAP for peaches with a residue of 0.36 mg/kg at 7 days provided supporting information. A single Chilean trial on nectarines reflected the Argentinian GAP for peaches (0.072 kg ai/ha, PHI 20 days) with no residue detected. No data on supervised trials were available for Japanese GAP in which there is a 1-day PHI.

Table 26. Supervised residue trials on peaches, apricots and nectarines.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Fronton, S. France, 1993[1]	EC	3	0.04	0.0078	0	pulp	0.13	NG 07 R93-46
					6		0.04	
					10		0.06	
					13		0.04	
Fronton, France, 1994	EC	5	0.04	0.008	8	pulp	0.03	NG 11 GHE-P-4062
Follonica, Italy, 1977[2-6]	WP	8		0.0042	34	fruit	<0.01	NG 01 I77-212A
Puntone, Italy, 1977[2-6]	WP	4		0.0042	20	fruit	0.02	NG 02 I77-213
Follonica, Italy, 1977[2-6]	WP	6	0.24	0.0042	16	fruit	<0.01	NG 03 I77-214
S. Biagio, Italy, 1993[1]	SC	5	0.09	0.0042	0	pulp	0.44	NG 08 R93-45
					7		0.13	
					10		0.08	
					14		0.08	
			0.1	0.0048	0	pulp	0.65	
					7		0.15	
					10		0.15	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					14		0.16	
Francolino, Italy, 1994	SC	4	0.066 0.069 0.071 0.072	0.0048 x 4	13	pulp	0.05	NG 10 GHE-P-4014
Luchente, Spain, 1988[2,3,5,6,7]	EC	1	0.18	0.0048	0	fruit	0.41	ref. 13
					3		0.38	
					7		0.30	
					14		0.12	
					21		0.10	
Pobla del Duc, Spain, 1992[2,3,5,6,7]	EC	1		0.0036	0	fruit	0.18	ref. 13
					7		0.08	
					14		0.03	
					21		0.02	
Pobla del Duc, Spain, 1993[2,3,5,6,7]	EC	1		0.0036	0	fruit	0.07	ref. 13
					7		0.03	
					14		0.02	
					21		0.01	
NECTARINE								
Chile[2,5,7]	EC		0.072	0.0036	0	fruit	0.03	NG 09
					6		<0.01	
					16		ND	
					24		ND	
APRICOT								
Luchente, Spain, 1988[2,3,5,6,7]	EC	1	0.18	0.0048	0	fruit	0.45	ref. 13
					3		0.44	
					7		0.36	
					14		0.14	
					21		0.08	

Underlined residues are from treatments according to GAP in Spain
Results underlined twice reflect GAP in Argentina
ND - not detected
[1] Crops stored for 11 months before analysis
[2] No weather data submitted
[3] Method of analysis unspecified (reports 2, 3, 4 & 5 in Spanish
[4] Low associated recoveries (NG01 69%; NG02 68%; NG03 59%
[5] No example chromatograms submitted
[6] Duration of sample storage unspecified
[7] No English translation provided

Cherries. GAP was reported for Denmark, Japan and the USA. The maximum application rates reported were 0.06 to about 0.2 kg ai/ha with PHIs of 0-14 days.

All 15 trials submitted were from the USA with samples being taken at 0 and 1 day after the final treatment. In all these trials no account was taken of the weights of the stones. US GAP (0.101 kg ai/ha) allows treatment 'up to and after harvest' and residues in the 9 trials (3 of which were replicated) complying with it were 0.06-0.89 mg/kg.

Table 27. Supervised residue trials on cherries in the USA.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Traverse City, MI, 1987[1,2]	EC	6	0.053		0	fruit pulp	0.21	NG 04 87MI1
					1		0.24	
Geneva, NY, 1987[1,2]	EC	5	0.095		0	pulp	0.07	NG 04 87NY1
					1		0.10	
Biglerville, PA, 1987[1,2]	EC	5	0.089		0	pulp	0.10	NG 04 87PA1
					1		0.11	
Hart, MI, 1987[1,2]	EC	5	0.053		0	fruit	0.16	NG 04 WWH87-2
					1		0.17	
Hart, MI, 1987[1,2]	EC	5	0.053		0	pulp	0.18	NG 04 WWH87-3
					1		0.13	
Sutton Bay, MI, 1987[1,2]	EC	5	0.053		0	pulp	0.28	NG 04 WWH87-5
					1		0.26	
Sutton Bay, MI, 1987[1,2]	EC	6	0.053		0	pulp	0.20	NG 04 WWH87-6
					1		0.10	
Sutton Bay, MI, 1987[1,2]	EC	5	0.053		0	pulp	0.17	NG 04 WWH87-7
					1		0.16	
Vantage Bay, WA, 1987[1,2]	EC	4	0.105		0	pulp	0.06	NG 04 WTC87-3
					1		0.05	
Malago, WA, 1987[1,2]	EC	4	0.105		0	pulp	0.44	NG 04 WTC87-6
					1		0.41	
Othello, WA, 1987[1,2]	EC	4	0.105		0	pulp	0.17	NG 04 WTC87-7
					1		0.15	
Corvallis, MI, 1987[1,2]	EC	4	0.105		0	pulp	0.63	NG 04 WTC87-8
					1		0.64	
Linden, CA, 1989	EC	4	0.106		0	fruit	0.89	NG 05 LES89-05
					1		0.49	
			0.106	0.0056	0	fruit	0.77	
					1		0.63	
Grevais. OR, 1989	EC	4	0.106	0.0056	0	fruit	0.22	NG 05 LR89-01
					1		0.28	
	SC	4	0.106	0.0056	0	fruit	0.1	
					1		0.1	
Westley, CA,1989	EC	4	0.106	0.0056	0	fruit	0.4	NG 05 LES89-04
					1		0.88	
	SC	4	0.106	0.0056	0	fruit	0.3	
					1		0.25	

Underlined residues are from treatments according to GAP in the USA
[1] No weather data submitted
[2] Duration of sample storage unspecified

Currants. GAP for blackcurrants was reported for Denmark, Ireland and the UK, and for all currants for The Netherlands. The application rates were 0.04-0.06 kg ai/ha or 0.0048 kg ai/hl with PHIs of 14 or 21 days.

Data were available only from 5 trials in The Netherlands. Residues were 0.04-0.74 mg/kg 15 days after the final treatment but with a variety of application rates with only one trial according to the reported GAP.

Gooseberries. GAP in Ireland and The Netherlands is the same as for currants. Only one trial in The Nethlands was reported with a residue of 0.05 mg/kg at 10 days and this trial was submitted in summary form only.

Table 28. Supervised residue trials on currants and gooseberries in The Netherlands in 1980. All EC applications. All reference 6.

Crop	Application			PHI, days	Residues, mg/kg
	No.	kg ai/ha	kg ai/hl		
Blackcurrant[1,2]					
	8		40ppm	2	0.1
				10	0.07
				14	0.04
				22	0.05
				29	0.06
	1	6-	60 ppm	13	0.47
	1		80 ppm	13	0.45
	?	0.06		50	0.10
	?	0.08		13	0.74
Redcurrant[1,2]					
	3	0.048		25	0.07
					0.14
					0.06
					0.08
Gooseberry[1,2]					
	8		40ppm	2	0.07
				10	0.05

Underlined residues are from treatments according to GAP in The Netherlands
[1] No example chromatograms submitted
[2] No English translation provided

Grapes. GAP was reported for many countries world-wide. The maximum application rates were 0.012-0.06 kg ai/ha with PHIs of 7-35 days.

Residue trials were available from Germany, France, Austria, Italy, the USA, Brazil and Australia. A number of German trials were submitted of which six (2 with replicates) were according to German GAP (0.0234 kg ai/ha, 35-day PHI). The residues in these were 0.01-0.15 mg/kg in samples taken 35 days after the final treatment. Seven of the German trials (two with replicates) were at or within the UK GAP (0.04 kg ai/ha, PHI of 14 days) with residues of 0.02-0.24 mg/kg in samples taken 14 days after the final treatment. In a single French trial conducted in accordance with GAP in France (0.018 kg ai/ha, PHI 7 days) a residue of 0.02 mg/kg was found after 9 days.

Residues in trials according to US GAP (0.051 kg ai/ha, 30-day PHI) were low (0.003-0.06 mg/kg) in 17 US trials, several of which were replicated, in samples taken 28-32 days after the final treatment. Australian GAP (0.024 kg ai/ha or 0.0024 kg ai/hl, 14-day PHI) was also supported by 5 trials with either the maximum spray concentration or application rate per hectare (both are stated on the product label). Residues were 0.01-0.08 mg/kg 13 or 14 days after the final treatment.

None of the Southern European trials according to GAP conformed to Italian (0.06kg ai/ha or 0.0036 kg ai/hl, 14-day PHI) or Portuguese GAP (0.03kg ai/ha or 0.003 kg ai/hl, 7-day PHI) which have the highest dose rate and the shortest PHI respectively.

Table 29. European supervised residue trials on grapes.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Rohrendorf, Austria, 1977[1,2,5,6]	EC	4	0.036	0.0036	58	fruit	<0.01	NH 05
Rohrendorf, Austria, 1977[1,2,5,6]	WP	4	0.036	0.0036	58	fruit	0.01	NH 05
Grosshofflein, Austria, 1977[1,2,5,6]	EC	4	0.024	not reported	66	fruit	0.02	NH 06
		4	0.036	0.0036	66	fruit	<0.01	
Pau, France, 1981[5]	SC	4	0.024	0.024 Low vol.	0	fruit	0.18	NH 12
					7	fruit	0.12	
					14	fruit	0.05	
		4	0.036	0.036 Low vol.	0	fruit	0.27	
					7	fruit	0.18	
					14	fruit	0.04	
Sistels, France, 1993[3]	SC	3	0.018	0.075 Low vol.	0	fruit	0.04	NH 04
					4	fruit	0.03	
					9	fruit	0.02	
					15	fruit	0.02	
Godramstein, Germany, 1992[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.02	NH 11
					35	fruit	0.03	
					42	fruit	0.01	
					35	must	<0.01	
					35	wine	<0.01	
Londau, Germany, 1992[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.04	NH 11

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
					35	fruit	0.04	
					42	fruit	0.02	
					35	must	<0.01	
					35	wine	<0.01	
Neustadt, Germany, 1993[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.02	NH 11
					35	fruit	0.01	
					42	fruit	0.02	
					35	must	<0.01	
					35	wine	<0.01	
Neustadt, Germany, 1993[3]	SC	6	0.003+ 0.005+ 0.014+ 0.018+ 0.020+ 0.025	0.0008+ 0.0008+ 0.0026+ 0.0031+ 0.0036+ 0.0042	28	fruit	0.02	NH 11
					35	fruit	0.02	
					42	fruit	0.01	
					35	must	<0.01	
					35	wine	<0.01	
Bad Kreuznach, Germany, 1982 [5]	SC	8	0.005-0.033	2X0.0016 6X0.0031	0	fruit	0.23	NH 12
					7	fruit	0.14	
					14	fruit	0.14*	
					21	fruit	0.10	
					28	fruit	0.11	
					35	fruit	0.07	
					42	fruit	0.08	
Ortsweil Wolf, Germany, 1982 [5]	EC	6	0.014-0.04	2X0.0008 4X0.0016	0	fruit	0.56	NH 12
					7	fruit	0.22	
					14	fruit	0.20*	
					21	fruit	0.10	
					28	fruit	0.07	
					35	fruit	0.06	
					42	fruit	0.05	
Ortsweil Wolf, Germany, 1982 [5]	SC	6	0.014-0.04	2X0.0008 4X0.0016	0	fruit	0.44	NH 12
					7	fruit	0.28	
					14	fruit	0.18*	
					21	fruit	0.10	
					28	fruit	0.07	
					35	fruit	0.05	
					42	fruit	0.05	
Trier, Germany, 1982 [5]	SC	6	2X0.012 4X0.024	2X0.0008 4X0.0016	0	fruit	0.02	NH 12

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
					7	fruit	0.03	
					14	fruit	0.02*	
					21	fruit	0.01	
					28	fruit	0.01	
					35	fruit	0.01	
					42	fruit	0.01	
		8	1X0.014 7X0.028	1X0.0008 7X0.0016	0	fruit	0.33	
					7	fruit	0.24	
					14	fruit	0.24*	
					21	fruit	0.23	
					28	fruit	0.19	
					35	fruit	0.15	
					42	fruit	0.14	
Trier, Germany, 1982 [5]	EC	6	2X0.012 4X0.024	2X0.0008 4X0.0016	0	fruit	0.03	NH 12
					7	fruit	0.02	
					14	fruit	0.02*	
					21	fruit	0.01	
					28	fruit	0.01	
					35	fruit	0.01	
					42	fruit	0.01	
		8	1X0.014 7X0.028	1X0.0008 7X0.0016	0	fruit	0.17	
					7	fruit	0.16	
					14	fruit	0.10*	
					21	fruit	0.09	
					28	fruit	0.09	
					35	fruit	0.10	
					42	fruit	0.11	
Thringen, Germany, 1982[5]		8	2X0.015 6X0.039	1X0.0008 7X0.0020	0	fruit	0.20	NH 12
					7	fruit	0.14	
					14	fruit	0.18*	
					21	fruit	0.11	
					28	fruit	0.08	
					35	fruit	0.08	
					42	fruit	0.08	
Bad Kreuznach, Germany, 1982[5]	EC	8	2X0.015 6X0.039	1X0.0008 7X0.0020	0	fruit	0.08	NH 12
					7	fruit	0.06	
					14	fruit	0.07*	
					21	fruit	0.05	
					28	fruit	0.03	
					42	fruit	0.05	
					35	fruit	0.03	
Calderara, Italy, 1977[1,2,4-6]	WP	7	0.024	not reported	22	fruit	0.02	NH 09

Underlined residues are from treatments according to GAP in Germany; the residue underlined twice was from treatment according to GAP in France
* according to UK GAP.
[1] No weather data submitted
[2] Method of analysis unspecified
[3] Crops stored for more than 6 months before analysis (8-9 months except wine samples)
[4] Low associated recoveries (63%)
[5] No example chromatograms submitted
[6] Duration of sample storage unspecified

Table 30. Non-European supervised residue trials on grapes (including US processing trials).

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
Sungarden, Australia, 1976[1,2]	EC	2	0.015	0.003	71	fruit	--	NH 22 AUS 76-237
		2	0.01	0.002	71	fruit	0.001	
		2	0.02	0.004	71	fruit	0.005	
Victoria, Australia, 1976[1,2,4]	EC	2	0.01	0.002	89	fruit	0.001	NH 22 AUS 76-238
		2	0.015	0.003	89	fruit	0.001	
		3	0.03	0.02	66	fruit	0.001	
		3	0.045	0.003	66	fruit	0.001	
		3	0.06	0.004	66	fruit	0.002	
Mclaren Vale, S. Australia, 1978[1,2]	EC	4	0.09	0.0036	90	fruit	0.009	NH 22 AUS 78-263
Pokolbin, NSW, Australia, 1980[1,2]	EC	7	0.01	0.001	8	fruit	0.05	NH 22 AUS 79-339
		7	0.024		8	fruit	0.06	
Mclaren Vale, S. Australia, 1981 (1,7)	EC	4		0.0024	0	fruit	0.34	NH 23 AUS 80-223
					1	fruit	0.19	
					5	fruit	0.09	
					29	fruit	0.02	
		4		0.0036	0	fruit	0.72	
					1	fruit	0.43	
					5	fruit	0.27	
					29	fruit	0.10	
Lyndoch, S. Australia, 1981[1,2]	EC	4	0.047	0.0024	0	fruit	0.28	NH 22 AUS 83-201
					7	fruit	0.22	
					14	fruit	<u>0.06</u>	
					28	fruit	0.02	
		4	0.094	0.0048	0	fruit	0.45	
					7	fruit	0.37	
					14	fruit	0.19	
					28	fruit	0.10	
Pokolbin, NSW, Australia, 1985[1,3]	EC	4		0.0024	7	fruit	0.02	NH 23 F/H01/85
					13	fruit	<u>0.01</u>	
					20	fruit	0.001	
					27	fruit	0.01	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
		4		0.0048	7	fruit	0.06	
Irymple, Australia, 1992[1,2,4]	EC	1	0.037	0.0024	0	fruit	1.01	NH 24 S93 FEN1
					1		0.84	
					3		0.46	
					7		0.11	
					14		0.06	
					22		0.03	
					35		<0.2	
Irymple, Australia, 1993[1,2,4]	EC	1	0.037	0.0024	0	fruit	0.23	NH 24 S93 FEN3
					1		0.2	
					3		0.16	
					7		0.08	
					14		0.05	
					21		0.03	
					14	wine	0.008	
					14	dried fruit	0.03	
Nuriootpa, Australia, 1993[1,2,4]	EC	1	0.024	0.040-0.074	0		0.06	NH 24 A93 FEN2
					1		0.06	
					3		0.18	
					5		0.05	
					7		0.05	
					14		0.08	
					21		0.05	
					28		0.04	
					28	wine	0.008	
Nuriootpa, Australia, 1993[1,2,4]	EC	6	0.048	0.080- 0.148	28	fruit	0.57	NH 24 A93 FEN4
Brazil, 1985[1,2,4,7]	EC	11	0.024	0.0024	28	fruit	0.03	NB 29
Fresno, CA, USA, 1981[1,2]	EC	4	0.019 0.028 0.037 0.037		62	fruit	0.008	NH 21 DHF81-3
Fresno, CA, USA, 1981[1,2]	EC	3	0.025 0.025 0.025		70	fruit	<0.002	NH 21 DHF81-4
		4	0.037 0.056 0.074		70	fruit	0.006	
		3	0.025 0.025 0.025		70	fruit	0.002	
		3	0.012 0.025 0.037		70	fruit	0.003	
Fresno, CA, USA, 1981[1,2]	SC	3	0.019 0.028 0.037		70	fruit	0.005	NH 21 DHF81-4
		3	0.037		70	fruit	0.005	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
			0.037 0.037					
		3	0.037 0.037 0.037		70	fruit	0.002	
			0.012 0.025 0.037		70	fruit		
Fresno, CA, USA, 1981[1,2]	SC	3	0.074 0.111 0.148		70	fruit	0.02	NH 21 DHF81-5
	EC	3	0.037 0.056 0.074		70	fruit	0.007	
Fresno, CA, USA, 1981[1,2]	EC	3	0.025 0.025 0.025		15	fruit	<0.002	NH 21 DHF81-6
	SC	3	0.05 0.05 0.05		15	fruit	0.008	
Fresno, CA, USA, 1981[1,2]	SC	3	0.05 0.05 0.05		119	fruit	<0.002	NH 21 LGT81-7
	EC	3	0.05 0.05 0.05		119	fruit	0.03	
Grandview, WA, USA, 1982[1,2]	EC	3	0.026		106	fruit	0.002	NH 17 82WA3
						juice/wine	<0.002	
						wet pomace	0.008	
						dried pomace	0.030	
Grandview, WA, USA, 1982[1,2]	EC	3	0.035		106	fruit	0.004	NH 17 82WA3
						juice/wine	<0.002	
						wet pomace	0.012	
						dried pomace	0.047	
Paw Paw, MI, USA, 1982[1,2]	EC	3	0.018 0.026 0.035		50	fruit	<0.002	NH 17 DE-082-31
						juice/wine	<0.002	
						wet pomace	0.003	
						dried pomace	0.012	
Paicines, CA, USA, 1983[1,2,5]	EC	2	0.044		94	fruit	0.006	NH 17 DF-83-62
						juice/wine	<0.002	
						wet pomace	0.011	
					94	fruit	0.005	
						juice/wine	<0.002	
						wet pomace	0.006	
					96	fruit	0.005	
						juice/wine	<0.002	
						wet pomace	0.005	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					96	fruit	0.006	
						juice/wine	<0.002	
						wet pomace	0.007	
Thermal, CA, USA, 1983[1,2,5]	EC	3	0.026 0.035 0.052		40	fruit	0.005	
						juice/wine	<0.002	
Thermal, CA, USA, 1983[1,2]	EC	3	0.026 0.035 0.052		40	fruit	0.005	NH 17 DHF-83-16
						juice/wine	<0.002	
						fruit	0.008	
		2	0.035 0.044		40	fruit	0.001	
Thermal, CA, USA, 1983[1,2]	EC	3	0.026 0.035 0.052		32	fruit	0.006	NH 17 DHF-83-17
	EC	3	0.026 0.035 0.052		32	fruit	0.007	
	SC	3	0.035 0.044 0.061		32	fruit	0.009	
Thermal, CA, USA, 1983[1,2]	EC	3	0.026 0.035 0.052		32	fruit	0.007	NH 17 DHF-83-18
	EC	3	0.026 0.035 0.052		32	fruit	0.003	
	SC	3	0.035 0.044 0.061		32	fruit	0.010	
Thermal, CA, USA, 1984	EC	3	0.025+ 0.033+ 0.05		47	fruit	<0.001	NH 02
		3	0.025+ 0.033+ 0.05		27	fruit	0.001	
		3	0.025+ 0.033+ 0.05		0	fruit	0.33	
					3	fruit	0.18	
					7	fruit	0.072	
					15	fruit	0.033	
					30	fruit	0.005	
Biola, CA, USA, 1984[1]	EC	2	0.033 0.05		82	fruit	0.004	NH 02 845-A
						juice	0.006	
						pomace	0.47	
						raisins	0.005	
						raisin waste	0.34	
Biola, CA, USA, 1984[1]	EC	3	0.025 0.033		82	fruit	0.004	NH 02 845-B

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
			0.05					
						juice	0.006	
						pomace	0.071	
						raisins	0.005	
						raisin waste	0.31	
Sanger, CA, USA, 1984[1]	EC	2	0.033 0.05	0.007 0.0107	86	fruit	0.006	NH 02 846-A
						juice	0.022	
						pomace	0.042	
						raisins	0.011	
						raisin waste	0.29	
Sanger, CA, USA, 1984[1,5]	EC	3	0.025 0.033 0.05	0.0053 0.007 0.0107	86	fruit	0.004	NH 02 846-B
						juice	0.008	
						pomace	0.035	
						raisins	0.004	
						raisin waste	0.52	
Biola, CA, USA, 1984[1]	EC	2	0.033 0.05	0.007 0.0107	92	fruit	0.004	NH 02 847-A
						juice	0.003	
						pomace	0.052	
Biola, CA, USA, 1984[1]	EC	3	0.025 0.033 0.05	0.0053 0.007 0.0107	92	fruit	0.003	NH 02 847-B
						juice	0.001	
						pomace	0.026	
Fresno, CA, USA, 1987	EC	4	0.025+ 0.033+ 0.05+ 0.05	0.0053+ 0.0071+ 0.0106+ 0.0106	30	fruit	0.03	NH 01
						juice	0.08	
						pomace	0.21	
		4	0.025+ 0.033+ 0.05+ 0.05	0.0053+ 0.0071+ 0.0106+ 0.0106	30	fruit	0.02	NH 01
						juice	0.07	
						pomace	0.19	
						raisin waste	0.48	
						raisins	0.04	
Biola, CA, USA, 1987[1]	EC	4	0.025 0.033 0.05 0.05	0.0053 0.0071 0.0106 0.0106	30	fruit	0.026	NH 01 87-13
						raisins	0.04	
						raisin waste	0.30	
Kerman, CA, USA, 1987[1]	EC	4	0.025 0.033 0.05 0.05		30	fruit	0.019	NH 01 87-14

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
						juice	0.047	
						pomace	0.09	
						raisins	0.04	
						raisin waste	0.26	
Bethlehem, PA, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	<0.042	NH 20 8804R
Phelps, NY, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	<0.006	NH 20 88060
Dundee, NY, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	<0.010	NH 20 88061
Sunnyside, WA, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	<0.033	NH 20 BJB88-05
Sunnyside, WA, USA, 1988	EC	4	0.025 0.033 0.05 0.05		30	fruit	<0.017	NH 20 BJB88-06
Fresno, CA, USA, 1988	EC	3	0.025 0.033 0.050		30	fruit	<0.007	NH 20 LE388-17
Biola, CA, USA, 1993[1,2]	EC	3	0.026 0.035 0.052		13	fruit	0.04	NH 17 DHF-83-56
					21	fruit	0.03	
					28	fruit	<0.016	
					45	fruit	0.009	
					61	fruit	0.01	
					13	juice	0.018	
					21	juice	0.011	
					28	juice	0.014	
					45	juice	0.012	
					61	juice	0.008	
					13	wet pomace	0.037	
					21	wet pomace	0.021	
					28	wet pomace	0.028	
					45	wet pomace	0.015	
					61	wet pomace	0.016	
		4	0.026 0.035 0.052 0.052		13	fruit	0.005	
					21	fruit	0.039	
					28	fruit	<0.032	
					45	fruit	0.015	
					61	fruit	0.017	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					13	juice	0.023	
					21	juice	0.013	
					28	juice	0.023	
					45	juice	0.016	
					61	juice	0.013	
					13	wet pomace	0.036	
					21	wet pomace	0.032	
					28	wet pomace	0.029	
					45	wet pomace	0.027	
					61	wet pomace	0.029	
Biola, CA, USA, 1993[1,2,5]	EC	3	0.026 0.035 0.052		14	fruit	0.023	NH 17 DHF-83-57
					21	fruit	0.024	
					28	fruit	0.019	
					45	fruit	0.021	
					59	fruit	0.009	
					14	juice	0.008	
					21	juice	0.012	
					28	juice	0.005	
					45	juice	0.003	
					59	juice	0.006	
					14	wet pomace	0.031	
					21	wet pomace	0.018	
					28	wet pomace	0.016	
					45	wet pomace	0.016	
					59	wet pomace	0.018	
					14	raisins	0.011	
					21	raisins	0.015	
					28	raisins	0.010	
					45	raisins	0.009	
					59	raisins	0.005	
					14	raisin waste	0.105	
					21	raisin waste	0.105	
					28	raisin waste	0.099	
					45	raisin waste	0.101	
					59	raisin waste	0.095	
		4	0.026 0.035 0.052 0.052		14	fruit	0.046	
					21	fruit	0.029	
					28	fruit	0.025	
					45	fruit	0.026	
					59	fruit	0.029	
					14	juice	0.008	
					21	juice	0.019	
					28	juice	0.008	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					45	juice	0.007	
					59	juice	0.009	
					14	wet pomace	0.027	
					21	wet pomace	0.026	
					28	wet pomace	0.027	
					45	wet pomace	0.019	
					59	wet pomace	0.019	
					14	raisins	0.017	
					21	raisins	0.019	
					28	raisins	0.014	
					45	raisins	0.010	
					59	raisins	0.012	
					14	raisin waste	0.171	
					21	raisin waste	0.191	
					28	raisin waste	0.179	
					45	raisin waste	0.131	
					59	raisin waste	0.206	
Sanger, CA, USA, 1993[1,2]	EC	4	0.026 0.035 0.052 0.052		16	fruit	0.053	NH 17 DHF-83-58
					21	fruit	0.053	
					30	fruit	0.043	
					48	fruit	0.081	
					63	fruit	0.032	
					16	raisin waste	0.347	
					21	raisin waste	0.401	
					30	raisin waste	0.216	
					48	raisin waste	0.332	
					63	raisin waste	0.271	
					16	juice	0.022	
					21	juice	0.025	
					30	juice	0.009	
					48	juice	0.017	
					63	juice	0.014	
					16	wet pomace	0.04	
					21	wet pomace	0.04	
					30	wet pomace	0.037	
					48	wet pomace	0.06	
					63	wet pomace	0.044	
					16	raisins	0.026	
					21	raisins	0.021	
					30	raisins	0.016	
					48	raisins	0.020	
					63	raisins	0.014	
Sanger, CA, USA, 1993[1,2]	EC	3	0.026 0.035 0.052		16	fruit	0.023	NH 17 DHF-83-58

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					21	fruit	0.024	
					30	fruit	0.016	
					48	fruit	0.024	
					63	fruit	0.024	
					16	raisin waste	0.178	
					21	raisin waste	0.157	
					30	raisin waste	0.111	
					48	raisin waste	0.177	
					63	raisin waste	0.124	
					16	juice	0.021	
					21	juice	0.019	
					30	juice	0.016	
					48	juice	0.015	
					63	juice	0.006	
					16	wet pomace	0.067	
					21	wet pomace	0.023	
					30	wet pomace	0.052	
					48	wet pomace	0.045	
					63	wet pomace	0.024	
					16	raisins	0.009	
					21	raisins	0.007	
					30	raisins	0.011	
					48	raisins	0.007	
					63	raisins	0.009	
Biola, CA, USA, 1993[1,2,5]	SC	3	0.035 0.052 0.061		14	fruit	0.024	NH 17 DHF-83-57
					21	fruit	0.028	
					28	fruit	0.040	
					45	fruit	0.020	
					59	fruit	0.009	
					14	juice	0.036	
					21	juice	0.023	
					28	juice	0.027	
					45	juice	0.014	
					59	juice	0.014	
					14	wet pomace	0.042	
					21	wet pomace	0.023	
					28	wet pomace	0.035	
					45	wet pomace	0.023	
					59	wet pomace	0.035	
					14	raisins	0.020	
					21	raisins	0.019	
					28	raisins	0.013	
					45	raisins	0.012	
					59	raisins	0.012	
					14	raisin waste	0.242	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					21	raisin waste	0.195	
					28	raisin waste	0.174	
					45	raisin waste	0.152	
					59	raisin waste	0.163	
Biola, CA, USA, 1993[1,2,5]	SC	4	0.035 0.052 0.061 0.070		14	fruit	0.068	NH 17
					21	fruit	0.052	
					28	fruit	0.044	
					45	fruit	0.040	
					59	fruit	0.044	
					14	juice	0.037	
					21	juice	0.038	
					28	juice	0.050	
					45	juice	0.021	
					59	juice	0.021	
					14	wet pomace	0.050	
					21	wet pomace	0.033	
					28	wet pomace	0.067	
					45	wet pomace	0.047	
					59	wet pomace	0.038	
					14	raisins	0.042	
					21	raisins	0.050	
					28	raisins	0.026	
					45	raisins	0.023	
					59	raisins	0.022	
					14	raisin waste	0.330	
					21	raisin waste	0.406	
					28	raisin waste	0.361	
					45	raisin waste	0.284	
					59	raisin waste	0.290	
Biola, CA, USA, 1993[1,2]	SC	3	0.035 0.052 0.061		13	fruit	0.061	NH 17 DHF-83-56
					21	fruit	0.024	
					28	fruit	0.029	
					45	fruit	0.041	
					61	fruit	0.019	
					13	juice	0.044	
					21	juice	0.015	
					28	juice	0.027	
					45	juice	0.028	
					61	juice	0.023	
					13	wet pomace	0.039	
					21	wet pomace	0.033	
					28	wet pomace	0.031	
					45	wet pomace	0.030	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
					61	wet pomace	0.028	
Biola, CA, USA, 1993[1,2]	SC	4	0.035 0.052 0.061 0.070		13	fruit	0.061	NH 17 DHF-83-56
					21	fruit	0.038	
					28	fruit	0.053	
					45	fruit	0.060	
					61	fruit	0.039	
					13	juice	0.043	
					21	juice	0.032	
					28	juice	0.094	
					45	juice	0.064	
					61	juice	0.053	
					13	wet pomace	0.052	
					21	wet pomace	0.037	
					28	wet pomace	0.053	
					45	wet pomace	0.055	
					61	wet pomace	0.057	
Sanger, CA, USA, 1993[1,2]	SC	3	0.035 0.052 0.061		16	fruit	0.067	NH 17 DHF-83-58
					21	fruit	0.032	
					30	fruit	0.061	
					48	fruit	0.061	
					63	fruit	0.021	
					16	juice	0.040	
					21	juice	0.039	
					30	juice	0.032	
					48	juice	0.031	
					63	juice	0.016	
					16	wet pomace	0.048	
					21	wet pomace	0.042	
					30	wet pomace	0.030	
					48	wet pomace	0.036	
					63	wet pomace	0.041	
					16	raisins	0.024	
					21	raisins	0.050	
					30	raisins	0.019	
					48	raisins	0.015	
					63	raisins	0.012	
					16	raisin waste	0.384	
					21	raisin waste	0.492	
					30	raisin waste	0.337	
					48	raisin waste	0.362	
					63	raisin waste	0.312	
Sanger, CA, USA, 1993[1,2]	SC	4	0.035 0.052		16	fruit	0.100	NH 17 DHF-83-58

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Reference
	Form	No.	kg ai/ha	kg ai/hl				
			0.061 0.070					
					21	fruit	0.053	
					30	fruit	0.085	
					48	fruit	0.060	
					63	fruit	0.034	
					16	juice	0.076	
					21	juice	0.034	
					30	juice	0.045	
					48	juice	0.044	
					63	juice	0.034	
					16	wet pomace	0.053	
					21	wet pomace	0.039	
					30	wet pomace	0.049	
					48	wet pomace	0.051	
					63	wet pomace	0.046	
					16	raisins	0.064	
					21	raisins	0.059	
					30	raisins	0.034	
					48	raisins	0.036	
					63	raisins	0.042	
					16	raisin waste	1.18	
					21	raisin waste	0.88	
					30	raisin waste	0.74	
					48	raisin waste	1.07	
					63	raisin waste	0.62	

Underlined residues are from treatments according to GAP in the USA; those underlined twice from treatments according to GAP in Australia

[1] No weather data submitted

[2] Duration of sample storage unspecified (Californian trials: 11 months maximum by calculation)

[3] NH23 F/H01/85 samples stored for 15 months

[4] No example chromatograms submitted

[5] Some high associated recoveries (NH 02 fruit, 122%; DHF 83-57 pomace, 123%, 136%; DHF 83-62 pomace 125%), but mean recoveries acceptable

[6] No detailed report submitted

[7] No English translation provided

Strawberries. GAP was reported for Denmark, Ireland, Italy, Japan (indoor and outdoor), The Netherlands, Spain and the UK. The maximum application rates are 0.03-0.084 kg ai/ha with PHIs of 1-14 days.

Data were available from Italy, Japan, Spain and The Netherlands. Two Italian trials and one Spanish trial were according to Italian GAP (0.048 kg ai/hl, 7-day PHI), with residues of 0.12-0.18 mg/kg. Spanish GAP has a PHI of 3 days (0.0048 kg ai/hl) and was only represented by the single Spanish trial with a residue of 0.25 mg/kg. at 3 days. Three Dutch trials were according to GAP (0.084 kg ai/ha, treatment before flowering) with residues of <0.01-0.02 mg/kg, but all the Dutch trials were submitted in summary form only. Japanese indoor GAP (0.003 kg ai/hl, 1-day PHI) was represented by 7 trials in which the crops were all protected by what was described as "vinyl housing cultivation with plastic mulch on bed". Residue levels in the trials were 0.04-0.56 mg/kg in samples taken 1 day after the final treatment.

Raspberries. Information on GAP was reported for Ireland and the UK. The application rate is 0.04 kg ai/ha with a PHI of 14 days. Only one trial was available from the UK, and this was at an exaggerated application rate.

Table 31. Supervised residue trials on strawberries and raspberries.

Location, year	Application					PHI, days	Residues, mg/kg	Ref.
	Sample	Form	No.	kg ai/ha	kg ai/hl			
STRAWBERRY								
Grosseto, Italy, 1979[1,2,3,5]	Field	WP	3	0.042	0.0042	7	0.12	NC 11
						16	0.09	
						22	0.07	
Grosseto, Italy, 1979[1,2,3,5]	Field	WP	3	0.042	0.0042	7	0.14	NC 12
						16	0.10	
						22	0.05	
Nara Pref., Japan, 1984[1,3]	Protected	WP	3	0.045	0.003	1	0.32**	NC16
						3	0.17	
						8	0.29	
Chiba Pref., Japan, 1984[1,3]	Protected	WP	3	0.045	0.003	1	0.43**	NC 16
						3	0.48	
						6	0.44	
Saitama Pref, Japan, 1987[1,3]	Protected	WP	3	0.06	0.003	1	0.04**	NC 16
Wakayama, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.13**	NC 16
Hyogo, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.56**	NC 16
Osaka, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.20**	NC 16
Shiga Pref, Japan, 1988[1,3]	Protected	WP	3	0.045	0.003	1	0.21**	NC 16
Ophensden, Netherlands, 1979[6]	Field	EC	1	0.084		238	0.02	6
Zaltbommel, Netherlands, 1979[6]	Field	EC	1	0.084		239	<0.01	6
Zundert, Netherlands, 1979[6]	Field	EC	1	0.084		238	<0.01	6
Breda, Netherlands, 1982[6]	Field	EC	1	0.07		15	<0.01	6
Vilanova de Castello, Spain, 1986[1,3,4,7]	Field	EC	3	0.096	0.0048	0	0.3	13
						3	0.25*	
						7	0.18	
						14	0.1	
						21	0.07	
RASPBERRY								
Earl Wood, Windlesham, UK, 1994[1,2,4]	Field	SC	3	0.075	0.0036	11	0.05	ND 01

Underlined residues are from treatments according to GAP in Italy; those underlined twice from treatments according to GAP in The Netherlands

* According to GAP in Spain
** According to Japanese indoor GAP
[1] No weather data submitted
[2] Method of analysis unspecified
[3] No example chromatograms submitted
[4] Duration of sample storage unspecified
[5] Crop variety unspecified
[6] No detailed report submitted
[7] No English translation provided

Bananas. GAP was reported for Honduras and Nicaragua. The application rates in both countries are 0.08-0.12 kg ai/ha with a PHI of 0 days.

Data were available from Ecuador, Costa Rica, Honduras and the Philippines. In all trials a low-volume application (20-48 l/ha) was made using a motorized backpack sprayer. Six trials reflected the use in Honduras and Nicaragua with residues 0 or 1 day after the final treatment of <0.01-0.19 mg/kg in unbagged bananas and <0.01-0.12 mg/kg in bagged bananas. Six further trials at twice the maximum application rate (i.e. 0.24 kg ai/ha) were also available with residues of 0.03-0.3 mg/kg in unbagged bananas and <0.01-0.12 mg/kg in bagged bananas.

Table 32. Supervised residue trials on bananas in 1992. All with 7 applications of EC.

Location, year	Application		Sample	Bagged/Un-bagged	PHI, days	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl					
Limon, Costa Rica -East	0.12	0.55	whole	unbagged	0	0.02	NL 02
			pulp	unbagged	0	0.02	
			whole	unbagged	1	0.02	
			pulp	unbagged	1	0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Limon, Costa Rica -East	0.24	1.1	whole	unbagged	0	0.03	NL 02
			pulp	unbagged	0	0.03	
			whole	unbagged	1	0.03	
			pulp	unbagged	1	0.05	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	0.01	
			pulp	bagged	1	<0.01	
Limon, Costa Rica -West	control		whole	bagged	-	<0.01 0.01	NL 02
	0.12	0.55	whole	unbagged	0	0.03	
			pulp	unbagged	0	0.01	
			whole	unbagged	1	0.03	
			pulp	unbagged	1	<0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Limon, Costa Rica -West	control	control	whole	bagged	-	<0.01 0.01	NL 02

Location, year	Application		Sample	Bagged/Un-bagged	PHI, days	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl					
	0.24	1.1	whole	unbagged	0	0.05	
			pulp	unbagged	0	-	
			whole	unbagged	1	0.05	
			pulp	unbagged	1	0.01	
			whole	bagged	0	0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Guayas, Ecuador Site 1	0.12	0.6	whole	unbagged	0	0.09	NL 02
			pulp	unbagged	0	0.05	
			whole	unbagged	1	0.19	
			pulp	unbagged	1	0.02	
			whole	bagged	0	0.12	
			pulp	bagged	0	0.01	
			whole	bagged	1	0.02	
			pulp	bagged	1	0.12	
Guayas, Ecuador Site 1	0.24	1.2	whole	unbagged	0	0.25	NL 02
			pulp	unbagged	0	0.12	
			whole	unbagged	1	0.22	
			pulp	unbagged	1	0.11	
			whole	bagged	0	0.02	
			pulp	bagged	0	0.01	
			whole	bagged	1	0.03	
			pulp	bagged	1	0.01	
Guayas, Ecuador Site 2	0.12	0.6	whole	unbagged	0	0.12	NL 02
			pulp	unbagged	0	0.11	
			whole	unbagged	1	0.16	
			pulp	unbagged	1	0.04	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	0.01	
			pulp	bagged	1	0.02	
Guayas, Ecuador Site 2	0.24	1.2	whole	unbagged	0	0.05	NL 02
			pulp	unbagged	0	0.07	
			whole	unbagged	1	0.3	
			pulp	unbagged	1	0.12	
			whole	bagged	0	0.04	
			pulp	bagged	0	0.03	
			whole	bagged	1	0.04	
			pulp	bagged	1	0.04	
La Lima, Honduras Site 1	0.12	0.00025	whole	unbagged	0	0.01	NL 02
			pulp	unbagged	0	<0.01	
			whole	unbagged	1	<0.01	
			pulp	unbagged	1	<0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	

Location, year	Application		Sample	Bagged/Un-bagged	PHI, days	Residues, mg/kg	Ref.
	kg ai/ha	kg ai/hl					
			pulp	bagged	1	<0.01	
La Lima, Honduras Site 1	0.24	0.5	whole	unbagged	0	0.02	NL 02
			pulp	unbagged	0	0.02	
			whole	unbagged	1	0.02	
			pulp	unbagged	1	0.02	
			whole	bagged	0	<0.01	
			pulp	bagged	0	<0.01	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
La Lima, Honduras Site 2	0.12	0.25	whole	unbagged	0	<0.01	NL 02
			pulp	unbagged	0	<0.01	
			whole	unbagged	1	0.01	
			pulp	unbagged	1	0.01	
			whole	bagged	0	<0.01	
			pulp	bagged	0	ND	
			whole	bagged	1	<0.01	
			pulp	bagged	1	ND	
La Lima, Honduras -Site 2	0.24	0.5	whole	unbagged	0	0.02	NL 02
			pulp	unbagged	0	<0.01	
			whole	unbagged	1	0.02	
			pulp	unbagged	1	0.02	
			whole	bagged	0	<0.01	
			pulp	bagged	0	0.02	
			whole	bagged	1	<0.01	
			pulp	bagged	1	<0.01	
Philippines[1]	0.15	0.11	pulp	NR	8	0.02	NL 03
			peel	NR	8	0.07	
			whole	NR	8	0.04	

Underlined residues are from treatments according to GAP in Honduras and Nicaragua
ND none detected
NR not recorded
[1] 1991

Cucumbers. GAP was reported for Brazil, Denmark, Ireland, Japan, The Netherlands, Uruguay and the UK. Several other countries reported GAP for the group "cucurbits". The maximum application rates are 0.019-0.072 kg ai/ha or 0.0012-0.0072 kg ai/hl with PHIs of 1-7 days.

Residue trials data were available from Austria, Italy, Brazil and the UK. One trial with a residue of 0.03 mg /kg was according to UK and Irish GAP (0.002 kg ai/hl, 2-day PHI) and a Brazilian trial with a residue at 4 days of 0.003 mg/kg complied with GAP in Uruguay. Residues in the Italian trials were at PHIs of 10-15 days, although this is longer than any reported GAP. There were no results at the Japanese GAP PHI of 1 day.

Gherkins. GAP was reported for The Netherlands (0.0024 kg ai/hl, 3-day PHI) for both protected and field use. Other countries had GAP for the group "cucurbits".

Two replicated Dutch trials were submitted in summary form in which a high application concentration of 0.24 kg ai/hl was reported, with the rate per hectare unspecified. Residues in samples taken 3 days after the final treatment were 0.02-0.06 mg/kg.

Table 33. Supervised residue trials on cucumbers and gherkins.

Location, year	Field protected	Application				PHI, days	Residues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
CUCUMBER								
Tadten, Austria, 1976[1,2,3,5]	Field	EC	1	0.012	0.0006	2	0.03	NB 01
		EC	1	0.024	0.0012	2	0.02	
Campinas, Brazil, 1986[1,3-5]	Field	EC	3	0.018		4	0.003	NB 29
			3	0.036		4	0.01	
Bellaria, Italy, 1977 [1-5]	Field	WP	8		0.003 high vol.	10	<0.01	NB 08
Borghesi, Italy, 1977 [1-5]	Field	WP	7		0.003 high vol.	22	<0.01	NB 09
Parma, Italy, 1981[1-3]	Field	SC	1	0.024	0.0024	15	<0.01	NB 15
Windlesham, Surrey, UK, 1976[1-3]	Protected	EC	6	250 ml/plant	0.002	2	0.03	NB 04
						4	0.05	
			6	250 ml/plant	0.004	2	0.09	
						4	0.07	
			6	250 ml/plant	0.008	2	0.03	
						4	0.16	
GHERKINS								
Denne, Netherlands, 1977[7]	Field?	EC	1		0.24	1	0.1	6
						3	0.03	
			1		0.24	1	0.07	
							0.05	
							0.1	
							0.08	
						3	0.06	
							0.03	

Location, year	Field protected	Application				PHI, days	Residues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
							0.05	
							0.02	
Wernhout, Netherlands, 1977[7]	Field?	EC	1		0.24	1	0.08	6
							0.06	
							0.1	
							0.05	
						3	0.06	
							0.04	
							0.03	
							0.02	

Underlined residues are from treatments according to GAP in UK and Ireland; those underlined twice from treatments according to GAP in Uruguay
[1] No weather data provided
[2] Method of analysis unspecified
[3] No example chromatograms submitted
[4] Duration of sample storage unspecified
[5] Crop variety unspecified
[6] No English translation provided
[7] No detailed report submitted

Melons (including cantaloupes) and watermelons. Indoor GAP for melons was reported for The Netherlands (0.0024 kg ai/hl, 3-day PHI), and outdoor GAP for melons for Japan, Portugal and Brazil and for watermelons for Japan, Brazil and Uruguay, as well as GAP for "cucurbits" in other countries. The maximum application rates are 0.012-0.036 kg ai/ha with PHIs of 1-7 days.

The only relevant indoor data were from two Spanish trials on melons but these were with a higher spray concentration than in Dutch GAP.

Outdoor trials were carried out on melons in France, Italy, Brazil and Spain, on watermelons in Italy and Brazil and on cantaloupes in Italy. In four French trials according to Greek GAP for cucurbits (0.024 kg ai/ha, 1-day PHI) residues were <0.01 and <0.01-0.11 mg/kg in the pulp and peel, respectively, 2 days after the final treatment. Residues at 4 days were <0.01 and 0.01-0.07 mg/kg in the pulp and peel respectively. When a double rate was applied (0.048 kg ai/ha) residues were only <0.01-0.02 and 0.04-0.09 mg/kg in the pulp and peel at 2 days. In these French trials the actual weights of pulp and peel were not recorded.

A number of other trials on melons in Brazil, Italy and Spain were at higher application rates than GAP at 0.036-0.048 kg ai/ha but residues were low (0.01-0.04 mg/kg) at 3-4 days. In a further three outdoor trials on watermelons in Italy and Brazil and two Italian trials on cantaloupes residues were all below the LOD (<0.01 mg/kg or ND) 4-14 days after the final treatment. Brazilian GAP (0.024 kg ai/ha, 4-day PHI) was represented by two trials; residues were 0.005 mg/kg in melons and "not detected" in watermelons, but in both trials the duration of sample storage was unspecified.

Table 34. Supervised residue trials on melons, watermelons and canteloupe melons.

Location, year	Field/ protected	Application				PHI, days	Sample	Residues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl				

Location, year	Field/ protected	Application				PHI, days	Sample	Res-idues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl				
MELON									
Campinas, Brazil, 1986[1,4-6]	Field	EC	3	0.018		4	whole	0.005	NB 29
			3	0.036		4	whole	0.04	
Savonieries, France, 1976[1,2,4]	Field	EC	3	0.01	0.0017	10	whole	<0.01	NB 02
			3	0.015	0.0025	10	whole	<0.01	
St Nicholas, France, 1980[1,2,4]		EC	1	0.024	0.0024	0	pulp	<0.01	NB 20
						0	pulp	<0.01	
						2	peel	0.03	
						2	peel	0.11	
						4	peel	0.06	
						4	peel	0.04	
Moissac, France, 1980 [1,2,4]	Field	EC	1	0.024	0.0025	0	pulp	<0.01	NB 21
						0	peel	0.09	
						2	pulp	<0.01	
						2	peel	0.03	
						4	pulp	<0.01	
						4	peel	0.01	
			1	0.048	0.0048	0	pulp	<0.01	
						0	peel	0.08	
						2	pulp	<0.01	
						2	peel	0.04	
						4	pulp	<0.01	
						4	peel	0.04	
St Nicola de la Grave, France, 1980[1,2,4]	Field	EC	1	0.024	0.0024	0	pulp	<0.01	NB 22
						0	peel	0.19	
						2	pulp	<0.01	
						2	peel	0.09	
						4	pulp	<0.01	
						4	peel	0.07	
			1	0.048	0.0048	0	pulp	0.01	
						0	peel	0.22	
						2	pulp	<0.01	
						2	peel	0.09	
						4	pulp	0.01	
						4	peel	0.08	
Moissac, France, 1980[1,2,4]	Field	EC	1	0.024	0.0022	0	pulp	<0.01	NB 23
						0	peel	<0.01	
						2	pulp	<0.01	
						2	peel	<0.01	
						4	pulp	<0.01	
						4	peel	0.04	
			1	0.048	0.0048	0	pulp	0.02	
						0	peel	013	
						2	pulp	0.02	
						2	peel	0.07	

Location, year	Field/ protected	Application				PHI, days	Sample	Res-idues, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl				
						4	pulp	<0.01	
						4	peel	0.04	
Volania, Ferrara, Italy, 1994	Field	SC	3	0.018+ 0.018+ 0.036	0.0036	7	peel	0.01	NB 32
						7	pulp	ND	
						7	whole	<0.01	
			3	0.024+ 0.024+ 0.048	0.0048	7	peel	0.01	
						7	pulp	ND	
						7	whole	<0.01	
Gavello, Italy, 1994	Field	SC	3	0.018+ 0.018+ 0.036	0.0036	7	peel	0.03	NB 32
						7	pulp	ND	
						7	whole	0.01	
			3	0.024+ 0.024+ 0.048	0.0048	7	peel	0.02	
						7	pulp	ND	
						7	whole	<0.01	
Los Alcazares, Spain, 1994	Protected	SC	3	0.037	0.0048	-1	whole	<0.01	NB 31
						0	whole	0.02	
						3	whole	0.02	
						5	whole	0.02	
						7	whole	<0.01	
Sevilla, Spain, 1994	Protected	SC	3	0.048	0.0048	-1	whole	<0.01	NB 31
						0	whole	0.01	
						3	whole	0.01	
						5	whole	<0.01	
						7	whole	0.01	
Romani, Spain, 1986[1,2,4,5,7]	Field	EC	2	0.096	0.0048	0	whole	0.1	13
						4	whole	0.07	
						7	whole	0.02	
						14	whole	ND	
CANTALOUPE MELONS									
Parma, Italy, 1977[1-6]	Field	WP	1	0.012	0.003	10	whole	<0.01	NB 11
Parma, Italy, 1981[1,2,4]	Field	SC	3	0.024	0.0024	14	whole	<0.01	NB 24
WATERMELONS									
Parma, Italy, 1976[1,2,4]	Field	EC	3	0.020	0.002	11	whole	<0.01	NB 03
Parma, Italy, 1977[1-4]	Field	WP	3		0.0018+ 0.0024+ 0.003	10	whole	<0.01	NB 12
Campinas, Brazil, 1986[1,4,6]	Field	EC	4	0.018	not reported	4	whole	ND	NB 29
			4	0.036	not reported	4	whole	ND	

Underlined residues are from treatments according to GAP in Greece; those underlined twice from treatments according to GAP in Brazil.

ND - not detected
[1] No weather data submitted
[2] Method of analysis unspecified
[3] Low associated recoveries (65% for cantaloupe trial, 68% for watermelon trial)
[4] No example chromatograms submitted
[5] Duration of sample storage unspecified
[6] Crop variety unspecified
[7] No English tranlation provided

Pumpkins, courgettes and squashes. GAP was reported for pumpkins for The Netherlands (indoor only), Brazil, Japan and Peru, for squash for Argentina (summer) and Uruguay, for courgettes for The Netherlands, and for "cucurbits" in other countries. The maximum application rates are 0.012-0.06 kg ai/ha with PHIs of 1-7days.

No data on indoor trials were submitted. One trial on squash in Brazil, complying with GAP for Argentina and Uruguay (0.024 kg ai/ha, 4 days PHI), showed a residue of 0.005 mg/kg. One Australian replicated trial on zucchini courgettes and one on pumpkins accorded with Australian GAP for curcurbits (0.024 kg ai/ha, 3-day PHI). Residues were very low; 0.001-0.01 mg/kg three days after the final treatment. The duration of laboratory sample storage was not given in the Australian trials considered to be according to GAP.

Table 35. Supervised residue trials on squash, zucchini, courgettes and pumpkins (whole commodities analysed).

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
SQUASH							
Campinas, Brazil, 1986[1,4,6]	EC	4	0.018	not reported	4	0.005	NB 29
		4	0.036	not reported	4	0.008	
Parma, Italy, 1977[1,2,3-6]	WP	3	0.12	0.003	15	<0.01	NB 10
Parma, Italy, 1981[1,2,4]	WP	4	0.024	0.0024	15	<0.01	NB 26
ZUCCHINI COURGETTES							
Pokolbin, NSW, Australia, 1985[1,5,6]			control	control	-	0.005	NB 30
	EC	4	0.01	not reported	3	0.01	
		4	0.02	not reported	3	0.01	
		4	0.03	not reported	3	0.02	
PUMPKINS							
Pokolbin, NSW, Australia, 1985[1,5,6]			control	control	-	0.001	NB 30
	EC	4	0.01	not reported	3	0.001	
		4	0.02	not reported	3	0.003	
		4	0.03	not reported	3	0.001	

Underlined residues are from treatments according to GAP for squash in Argentina and Uruguay; those underlined twice from treatments according to GAP for cucurbits in Australia
[1] No weather data provided
[2] Method of analysis unspecified
[3] Low associated recoveries (69%)
[4] No chromatograms submitted
[5] Duration of sample storage unspecified
[6] Crop variety unspecified

Tomatoes. GAP was reported for Denmark (glasshouse and field use), Italy, Japan, The Netherlands (glasshouse and field use), Spain and the UK. The maximum application rates are 0.036-0.072 kg ai/ha or 0.002-0.0048 kg ai/hl with PHIs of 1-7days.

Data were available from Italy, Spain, The Netherlands and Greece. Treatments in two Netherlands indoor trials were comparable to Danish GAP (0.036 kg ai/ha or 0.0048 kg ai/hl, 2-day PHI). Residues in both were 0.03 mg/kg at 2 days. Italian GAP (0.0048 kg ai/hl, 7-day PHI) and Spanish GAP (0.006 kg ai/hl, 7-day PHI) were reflected in one Spanish and two Italian trials with residues of 0.03, 0.03 and 0.05 mg/kg at 7days.

Peppers. GAP for peppers is the same as for tomatoes except that Denmark has no registered use.

Trials data were available from Italy, Spain and Israel. Spanish and Italian GAP (0.0048 or 0.006 kg ai/hl with a PHI of 7days) were represented by 6 trials in Italy and Spain. Residues were 0.03-0.07 mg/kg and 0.07-0.5 mg/kg respectively in samples taken 7 days after the final treatment. The duration of sample storage was not specified in the Spanish trials.

Egg plants (aubergines). Outdoor GAP was reported for Italy and Japan. The maximum application rates are about 0.04 kg ai/ha or about 0.002-0.0048 kg ai/hl with a PHI of 1 day in Japan and 7 days in Italy.

Only one Italian trial was reported, in which the residue was <0.01 mg/kg 15 days after harvest.

Table 36. Supervised residue trials on tomatoes, peppers and egg plants.

Location, year	Field/ protected	Application				PHI, days	Res, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
TOMATOES								
Thessaloniki, Greece, 1994	Protected	EC	3	0.026 2 x 0.048	3 x 0.004	31	0.03	NE 12 GHE-P-4012
Grosetto, Italy, 1979[1-3]	Field	WP	3	0.084	0.0042	7	0.03	NE 03 I79-251
						14	0.06	
						21	<0.01	
Grosetto, Italy, 1979[1-3,5]	Field	WP	3	0.084	0.0042	7	0.03	NE 07 I79-250
						14	<0.01	
						21	<0.01	
Parma, Italy, 1981[1-3]	Field	SC	3	0.048	0.0042-0.0048	15	<0.01	NE 09 I81-258
Huissen, Netherlands, 1994	Protected	SC	3	0.048	0.0024	0	0.04	NE 11 R94-062-01
						1	0.04	
						2	0.03	
						3	0.03	
Bemmel, Netherlands, 1994	Protected	SC	3	0.048	0.0024	0	0.03	NE 11 R94-062-02
						1	0.03	
						2	0.03	
						3	0.02	
Marzarron, Spain, 1993[1]	Field	EC	3	*c.*0.06-0.08	0.0048	0	0.08	NE 08 GHE-P-3653
						2	0.06	
						7	0.05	
PEPPERS								

Location, year	Field/ protected	Application				PHI, days	Res, mg/kg	Ref.
		Form	No.	kg ai/ha	kg ai/hl			
Yad Natan, Israel, 1977[1-3]	Field	EC	2	0.036		30	0.03	NE 04 ISL79-2
						16	0.04	
						14	0.04	
						7	0.08	
						0	0.13	
			2	0.072		30	0.02	
						16	0.03	
						14	0.09	
						7	0.01	
						0	0.32	
Grosetto, Italy, 1979[1-3]	Field	WP	3		0.0042	7	0.07	NE 05 I79-250
						14	0.12	
						21	0.02	
Grosetto, Italy, 1979[1-3]	Field	WP	3		0.0042	7	0.03	NE 06 I79-251
						14	0.01	
						21	0.03	
Parma, Italy, 1981[1-3]	Field	SC	3	0.048	0.0048	15	<0.01	NE 10 I81-259
Cartagena, Spain, 1977[1-3,7]	Field		3		0.0024	30	0.03	NE 02 E77-129
					0.003		0.03	
Benifaio, Spain, 1986[1,3,6,7]	Field	EC	3	0.108	0.006	0	0.3	Ref. 13
						4	0.15	
						7	0.07	
						14	ND	
						21	ND	
Sollana, Spain, 1987[1,3,4,6,7]	Field	EC	1	0.126	0.006	0	0.27	Ref. 13
						3	0.23	
						7	0.12	
						14	0.05	
						21	0.03	
Benifaio, Spain, 1992[1,3,4,6,7]	Field	EC	1	0.15	0.006	0	0.6	Ref. 13
						3	0.56	
						7	0.5	
						14	0.2	
						21	0.1	
Benifaio, Spain, 1993[1,3,4,6,7]	Field	EC	1	0.12	0.006	0	0.21	Ref. 13
						3	0.26	
						7	0.08	
						14	0.05	
						21	0.03	
EGG PLANTS (AUBERGINES)								
Parma, Italy, 1981[1-3,5]	Field	SC	3		0.008	15	<0.01	NB 27 I81-260

Underlined residues are from treatments according to GAP in Spain and Italy
[1] No weather data submitted
[2] Method of analysis unspecified
[3] No example chromatograms submitted

[4] Duration of sample storage unspecified
[5] Crop variety unspecified
[6] No English translation provided
[7] The meeting was informed that samples were analysed within 24 hours of receipt at the laboratory.

Beetroots and carrots. Only Dutch GAP for "vegetables" was reported (0.036 kg ai/ha or 0.0024 kg ai/hl, 3-day PHI). There was one Netherlands trial on each of these crops in which residues were <0.01-0.02 mg/kg in samples taken 27 days after treatment.

Table 37. Supervised residue trials on beetroots and carrots at Slootdorp, The Netherlands, in 1984. 2 x 0.06 kg ai/ha EC applied in both trials (No example chromatograms submitted and no English translation provided for either trial).

PHI, days	Sample	Residues, mg/kg	Ref.
27	Beetroots, whole, roots and soil removed	0.01	KVW267/CTB/PD
		0.01	
		0.01	
		0.02	
		0.02	
27	Carrots, whole, soil removed	<0.01	KVW268/CTB/PD
		<0.01	
		<0.01	
		<0.01	

Globe artichokes. GAP was reported only for Italy (0.0048 kg ai/hl or 0.038 kg ai/ha, 7-day PHI). Six Italian trials with residues of <0.01-0.06 mg/kg were considered to reflect GAP. In two of these (1979) the analytical recovery was low (61%). In a Spanish trial a higher residue of 0.26 mg/kg was found at 7 days, but a high volume of water (2,500 l/ha) was applied and the spray concentration was higher (0.006 kg ai/hl) than that registered in Italy.

Table 38. Supervised residue trials on globe artichokes.

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
Grosseto, Italy, 1979[1,24,5,7]		2	0.084	0.0042	7	<0.01	NI 01
					14	<0.01	
					21	<0.01	
Grosseto, Italy, 1979[1,2,4,5]	WP	3	0.084	0.0042	7	0.03	NI 02
					14	<0.01	
					21	<0.01	
Grosseto, Italy, 1981[1,2,6]	SC	3	0.048	0.0048	14	0.03	NB 28
			control	control	-	0.02	
Del Gardinia, Italy, 1994	SC	3	0.035-0.036	0.0036	-1	0.04	NI 05
					1	0.07	
					7	0.04	
					14	<0.01	
					21	<0.01	
Del Gardinia, Italy, 1994	SC	3	0.046-0.048	0.0048	-1	0.03	NI 05

Location, year	Application				PHI, days	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl			
					1	0.10	
					7	0.06	
					14	0.02	
					21	<0.01	
Sezze, Italy, 1994	SC	3	0.031-0.035	0.0036	-1	0.02	NI 05
					1	0.11	
					7	0.05	
					14	0.02	
					21	<0.01	
Sezze, Italy, 1994	SC	3	0.042-0.047	0.0048	-1	0.05	NI 05
					1	0.19	
					7	0.06	
					14	0.04	
					21	0.02	
L'Alcudia, Spain, 1987[1,6,8]	EC	1	0.153	0.006	0	0.42	Ref. 13
					3	0.33	
					7	0.26	
					14	0.14	
					21	0.09	

Underlined residues are from treatments according to GAP in Italy
[1] No weather data submitted
[2] Method of analysis unspecified
[3] No control plot data
[4] Crops stored for 19 months before analysis
[5] Low recoveries (61%)
[6] No example chromatograms submitted
[7] Crop variety not specified
[8] No English translation provided

Witloof chicory. Only Dutch GAP for "vegetables" was reported (0.036 kg ai/ha or 0.0024 kg ai/hl, 3-day PHI). In a single trial residues were <0.01 mg/kg in samples taken 60 days after harvest.

Table 39. Supervised residue trials on witloof chicory at Slootdorp, The Netherlands, in 1984. 2 x 0.06 kg ai/ha of EC. No example chromatograms submitted and no English translation provided.

Sample	PHI, days	Residues, mg/kg	Reference
Crop	60	<0.01	KVW266/CTB/PD
Roots, soil removed	60	<0.01	

Pecans. GAP was reported for the USA and Mexico. The maximum application rates are 0.098 and 0.108 kg ai/ha with a PHI of 30 days in the USA and pre-flowering application in Mexico.

Twelve trials were carried out in the USA in four of which (one replicated) the final applications (0.074-0.12 kg ai/ha) were comparable to the registered rate in the USA (0.098 kg ai/ha). Residues were <0.002 and <0.002-0.02 mg/kg in the kernels and shells respectively after 35-153 days. In a further series of trials in which an exaggerated application rate was used (0.15-0.32 kg ai/ha) residues were <0.002-0.02 and <0.002-0.16 in the kernels and shells in samples taken 17-55 days after treatment. In one of these trials the laboratory samples were stored for 11 months before analysis.

Table 40. Supervised residue trials (field) on pecans in the USA.

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
Byron, GA, 1981[1]	EC	10	0.148*	0.003	30	kernel	<0.002	NM 01
Albany, GA, 1981[1,2,3]	SC	14	0.197*		35-39	kernel	<0.002	NM 01 RBC 81-25
						shell	0.164	
	EC	14	0.197*		35-39	kernel	0.02	
					55	shell	0.155	
Byron, GA, 1982[1]	EC	9	0.158*		55	kernel	<0.002	NM 01 USDA
						shell	<0.002	
Albany, GA, 1982[1]	EC	17	0.149*		29	kernel	<0.002	NM 01 RBC 82-1
						shell	<0.002	
					43	kernel	<0.002	
						shell	<0.002	
Albany, GA, 1982[1]	EC	17	0.149*		17	kernel	<0.002	NM 01 RBC 1, 2-5
						shell	<0.002	
Fitzpatrick, AL, 1982[1]	EC	14	0.149*		43	kernel	<0.002	NM 01 RDH 82-3
						shell	0.01	
Blakely, GA, 1982[1]	EC	11	0.12		38	kernel	<0.002	NM 02 RBC 83-12
					84	kernel	<0.002	
					107	kernel	<0.002	
					155	kernel	<0.002	
			0.12		38	shell	<0.002	
					84	shell	<0.002	
					107	shell	<0.002	
					155	shell	<0.002	
Artesia, MS, 1983[1]	EC	6	0.14		124	kernel	<0.002	NM 02 MS UNI
						shell	0.008	
		6	0.094		124	kernel	<0.002	
						shell	0.002	
Albany, GA, 1983[1]	EC	5	0.14		171	kernel	<0.002	NM 02 RBC 83-15
						shell	<0.002	
			0.32*		171	kernel	<0.002	
						shell	<0.002	
Albany, GA, 1983[1]	EC	11	0.12		25	kernel	<0.002	NM 02 RBC 83-16
			0.08		71	kernel	<0.002	
			0.063		94	kernel	<0.002	
			0.045		142	kernel	<0.002	
			0.12		25	shell	<0.002	
			0.08		71	shell	<0.002	
			0.063		94	shell	<0.002	
			0.045		142	shell	<0.002	
Fitzpatrick, GA, 1983[1]	EC	7	0.074		153	kernel	<0.002	NM 02 RDH 83-10
			0.10			kernel	<0.002	
			0.14			kernel	<0.002	
			0.11			kernel	<0.002	
			0.074		153	shell	0.02	

Location, year	Application				PHI, days	Sample	Residues, mg/kg	Ref.
	Form	No.	kg ai/ha	kg ai/hl				
			0.10			shell	0.004	
			0.14			shell	0.007	
			0.11			shell	<0.002	
Montgomery, AL, 1983[1]	EC	7	0.074		136	kernel	<0.002	NM 02 RDH 83-11
			0.10			kernel	<0.002	
			0.14			kernel	<0.002	
			0.11			kernel	<0.002	
			0.074		136	shell	0.014	
			0.10			shell	0.013	
			0.14			shell	0.023	
			0.11			shell	<0.002	

Underlined results are according to the registered application rate in the USA but are at longer PHIs; those underlined twice are from treatments according to GAP in the USA including the PHI.
* exaggerated application rate
[1] No weather data submitted
[2] Crops stored for 11 months before analysis
[3] Low associated recoveries (shells 44%)

Hops. GAP was reported for Germany and Spain. The maximum application rate was either 0.06 kg ai/ha or 0.0015 kg ai/hl with a 10-day PHI in Germany and 0.0048 kg ai/hl with an unspecified PHIs in Spain.

Four trials in Germany were all conducted according to German GAP. Residues in dried hops harvested 10 days after the final treatment were 2.22-3.55 mg/kg. Samples were stored for 13 months before analysis. The results are shown in Table 41.

Table 41. Supervised residue trials on hops, beer and spent yeast in Germany, 1990. All trials with 4 x 0.06 kg ai/ha (0.0015 kg ai/hl) of WP.

Location, year	PHI, days	Sample	Residues, mg/kg	Ref.
Rohr[1,2]	10	fresh hops	0.65	NJ 01 R90-616
		dried hops	3.15	
		spent hops	0.12	
		beer	<0.01	
		spent yeast	0.02	
Rohr[1,2]	10	fresh hops	1.12	NJ 01 R90-61B
		dried hops	3.55	
		spent hops	0.23	
		beer	<0.01	
		spent yeast	0.02	
Steinbach[1,2]	10	fresh hops	0.63	NJ 01 R90-61A
		dried hops	2.34	
		spent hops	0.14	
		beer	<0.01	
		spent yeast	0.02	
Rohr[1,2]	10	fresh hops	0.72	NJ 01 R90-61D
		dried hops	2.22	

Location, year	PHI, days	Sample	Residues, mg/kg	Ref.
		spent hops	0.12	
		beer	<0.01	
		spent yeast	0.02	

Underlined residues are from treatments according to GAP in Germany
[1] No weather data submitted
[2] Crops stored up to 13 months before analysis

Other commodites. GAP was also reported for peas in Japan and Italy and wheat in Japan, but no trials data were submitted.

Feeding trials on cattle and pigs

Twelve cattle (White Face) and twelve crossbred pigs were fed for 28 days on a diet containing nominally 0.1, 0.3 or 1.0 ppm fenarimol. The actual levels of the active ingredient in the treated feed were lower, apparently owing to the extraction procedures in which dichloromethane was used. The animals were killed 6 hours after the final feed. Tissues samples were extracted with methanol-acetonitrile, and the filtered extract partitioned with dichloromethane/aqeous NaCl. A cleaned up dichloromethane extract was then analysed by GLC with an ECD. Average procedural recoveries were 78-95% and 86-109% from cattle and pigs respectively. The residue distribution in tissues, corrected for recoveries, were as shown in Table 42 (Koons *et al*., 1984).

Table 42. Fenarimol residues in cattle and pigs.

Animal feeding level, ppm	Residue, mg/kg				
	Liver	Kidney	Muscle, loin	Muscle, round	Fat
Cattle					
0.1	0.005- 0.006	0.01	0.01	0.01	0.01
0.3	0.005-0.03	0.01	0.01	0.01	0.01
1.0	0.04-0.05	0.006-0.007	0.01	0.01	0.01
Pigs					
0.1	0.003-0.007	0.01	0.01	0.01	0.003-0.004
0.3	0.007-0.01	0.01	0.01	0.01	0.007-0.01
1.0	0.01-0.03	0.005-0.01	0.01	0.01	0.01-0.03

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were submitted.

In processing

Apples. Samples of apples with incurred residues of fenarimol were processed into juice, wet pomace following juice extraction, apple sauce, wet pomace following sauce production, and dry pomace. Samples were analysed by the method of Griggs and Decker (1981). Recoveries were variable but acceptable. Individual results are shown in Table 24 and a summary is given in Table 43.

Table 43. Summary of the distribution of fenarimol residues in apple and processed products.

Residues, mg/kg					
Whole fruit	Juice	Wet pomace from juice	Sauce	Wet pomace from sauce	Dry pomace
<0.002-0.04	<0.002-0.003	0.009-0.14	<0.002-0.009	<0.002-0.2	0.01-0.7

The residues in the wet pomace suggest that the residues were originally mainly in the peel. The individual results show that residues were generally concentrated about 2-fold from wet pomace to dry pomace during juice production, about 1-8-fold from wet pomace from sauce to dry pomace, and roughly 2-8-fold from whole fruit to wet pomace from juice (Decker and Day, 1983).

The concentration of residues between whole fruit and dry pomace is shown in detail in Table 44. Samples from the Cornel, Penn Univ and Winchester trials were soak-washed before analysis of the whole apples. The mean analytical recovery associated with the dry pomace results in these trials was high at 132%.

Table 44. Effect on residues of the production of dry pomace from whole apples.

Residues, mg/kg		Concentration factor	Ref.
Whole apple	Dry pomace		
<0.002	0.014	>7	NF 18 Cornel
0.037	0.67	18	NF 18 Penn Univ
0.017	0.20	12	NF 18 Penn Univ
0.059	0.31	5	NF 18 Winchester
0.057	0.36	6	NF 18 Winchester
0.014	0.12	9	NF 18 CMR 82-10
0.008	0.16	20	NF 18 CMR 82-10
<0.002	0.012	>6	NF 18 CMR 82-11
<0.002	0.013	>7	NF 18 CMR 82-11
0.007	0.12	17	NF 18 CMR 82-16
0.007	0.098	14	NF 18 CMR 82-16
0.004	0.068	17	NF 18 CDR 6-16
Median concentration factor		14	
Mean concentration factor		11.5	
Concentration factors excluding the trials from Cornel,		median 14	

Residues, mg/kg		Concentration factor	Ref.
Whole apple	Dry pomace		
Penn. Univ. and Winchester		mean 12.9	

Grapes. Grapes with incurred residues of fenarimol were processed into must and wine. Samples were analysed by the methods of Butcher and Perkins (1992) and Butcher (1994a). Recoveries from all substrates were acceptable. Individual results are are shown in Table 29. A summary is given in Table 45 (Butcher and Wood, 1994c).

Table 45. Distribution of fenarimol residues in grapes and processed products.

Residue, mg/kg		
Grapes	Wine	Must
0.01-0.03	<0.01	<0.01
0.02-0.04	<0.01	<0.01
0.01-0.02	<0.01	<0.01

The US residue trials on grapes included processing. Juice, pomace, raisin waste and raisins were all analysed. Most of the residue after processing was associated with the raisin waste. Further details including the individual results are shown in Table 30 (Dow Elanco Ltd., undated refs. NHO1, NHO2; Day, 1984a).

The concentration of residues from grapes to raisins is shown in Table 46 and from grapes to dry pomace in Table 47.

Table 46. Effect on residues of the production of raisins.

Residues, mg/kg		Concentration factor	Reference
Grapes	Raisins		
0.02	0.040	2.0	NH 01
0.004	0.005	1.3	NH 02
0.006	0.011	1.8	NH 02
0.004	0.004	1.0	NH 02
0.026	0.040	1.5	NH 02
0.019	0.040	2.1	NH 02
0.023	0.011	0.5	NH 17
0.024	0.015	0.6	NH 17
0.019	0.010	0.5	NH 17
0.021	0.009	0.4	NH 17
0.009	0.005	0.6	NH 17
0.046	0.017	0.4	NH 17
0.029	0.019	0.7	NH 17
0.025	0.014	0.6	NH 17
0.026	0.010	0.4	NH 17
0.029	0.012	0.4	NH 17
0.053	0.026	0.5	NH 17
0.053	0.021	0.4	NH 17
0.043	0.016	0.4	NH 17

Residues, mg/kg		Concentration factor	Reference
Grapes	Raisins		
0.081	0.020	0.2	NH 17
0.032	0.014	0.4	NH 17
0.023	0.009	0.4	NH 17
0.024	0.007	0.3	NH 17
0.016	0.011	0.7	NH 17
0.024	0.007	0.3	NH 17
0.024	0.009	0.4	NH 17
0.024	0.020	0.8	NH 17
0.028	0.019	0.7	NH 17
0.040	0.013	0.3	NH 17
0.020	0.012	0.6	NH 17
0.009	0.012	1.3	NH 17
0.068	0.042	0.6	NH 17
0.052	0.050	1.0	NH 17
0.044	0.026	0.6	NH 17
0.040	0.023	0.6	NH 17
0.044	0.022	0.5	NH 17
0.067	0.024	0.4	NH 17
0.032	0.050	1.7	NH 17
.061	0.019	0.3	NH 17
0.061	0.015	0.2	NH 17
0.021	0.012	0.6	NH 17
0.100	0.064	0.6	NH 17
0.053	0.059	1.1	NH 17
0.085	0.034	0.4	NH 17
0.060	0.036	0.6	NH 17
0.034	0.042	1.2	NH 17
median concentration factor		0.6	

Table 47. Effect on residues of the production of dry grape pomace.

Residues, mg/kg		Concentration factor	Reference
Grapes	Dry grape pomace		
0.002	0.030	15	NH 17
0.004	0.047	12	
<0.002	0.012	>6	

In two Australian residue trials grapes were fermented into wine. The results are shown in Table 30 (NH 24). The residues in the wine were very low.

Hops. Samples of hops with incurred residues of fenarimol were processed into dried hops, beer and spent hops. Spent yeast following brewing was also analysed. Analyses were by the method of Butcher and Perkins (1992). Recoveries from all substrates were acceptable. The residues were as shown in Table 48.

Table 48. Distribution of fenarimol residues in hops and brewing products.

Residue, mg/kg				
Fresh hops	Dried hops	Spent hops	Beer	Spent yeast
0.63-1.12	2.22-3.55	0.12-0.23	0.01	0.02

Individual results (given in Table 41) showed a 3-5-fold increase in residues between fresh and dried hops and a roughly 15-25-fold decrease between dried hops and spent hops (Butcher and Perkins, 1991).

Residues in the edible portion of food commodities

Bananas. Several residue trials were carried out in which the residues in the pulp and whole bananas were determined separately. In one trial the peel was also analysed separately. Residues of fenarimol were found in the edible pulp, but were generally lower than in the peel. The results are given in Table 32 (Catta-Preta and Matos, 1993; Ishikura, 1991).

Melons. Several residue trials were carried out in which the pulp and peel were analysed separately. Residues in the pulp were low (≤0.02 mg/kg), although in most of the trials samples were taken up to 4 days after a single treatment. Details are given in Table 34.

Pecans. In thirteen US trials residues in the kernels and shells were determined separately. Residues in the edible kernels were all <0.002 mg/kg whereas residues in the shells were 0.002-0.164 mg/kg from trials at a variety of application rates. Individual results are given in Table 40 (Decker, 1983a, 1984).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Results of random monitoring analyses undertaken by the Australian Department of Primary Industries and Energy from 1st January 1989 to 30th June 1992 are shown below. Sampling of fruit and vegetables was of the whole commodity excluding stones, stems, crowns etc.

Table 49. Australian monitoring data for fenarimol.

Commodity	Residue, mg/kg	Number of samples
Apple	<0.01	45
	0.01-0.04	2
	0.05-0.1	1
	TOTAL	48
Fresh grapes	<0.01	165
	trace only	1
	0.01-0.02	10
	0.02-0.05	1

	TOTAL	177
Pears	<0.01	17
	0.01-0.04	2
	TOTAL	19

NATIONAL MAXIMUM RESIDUE LIMITS

The national MRLs listed below were reported to the Meeting.

Country	Crop	MRL, mg/kg	Ref.
Argentina	apples	0.01	ref. 1
	grapes	0.1	
	peach	0.1	
	pear	0.01	
	squash, small	0.1	
Australia	pome fruit	0.2	ref. 2
	fruiting vegetables/cucurbits	0.2	
	grapes	0.1	
Brazil	apple	0.05	ref. 1
	cucumber	0.05	
	grapes	0.05	
	muskmelon	0.05	
	pumpkin	0.05	
	watermelon	0.05	
European Union[1]	citrus fruit	0.02*	ref. 3
	tree nuts	0.02*	
	pome fruit	0.3	
	stone fruit	(A)[2]	
	grapes, table & wine	0.3	
	strawberries	0.3	
	raspberries	0.3	
	currants	1	
	gooseberries	1	
	all other berries and small fruit	0.02*	
	root and tuber vegetables	0.02*	
	bulb vegetables	0.02*	
	fruiting vegetables	(A)	
	brassica vegetables	0.02*	
	leaf vegetables	0.02*	
	peas with & without pods	(A)	
	other legumes	0.02*	
	artichokes	(A)	
	other stem vegetables	0.02*	
	fungi	0.02*	
	pulses	0.02*	
	oil seeds	0.02*	
	potatoes	0.02*	
	tea	0.01*	
	hops	5	
	wheat/barley	(A)	
	other cereals	0.02*	

Country	Crop	MRL, mg/kg	Ref.
	liver/kidney	(A)	
	other meat, milk or dairy	0.02*	
Hungary	apple	0.2	ref. 1
	blueberry/gooseberry	0.2	
	cherry	0.2	
	cucurbits	0.2	
	parsley	0.2	
	vineyards	0.2	
Japan	apple	1	
	aubergine	0.5	ref. 1
	cucumber	0.5	
	melon	1	
	pea, immature	0.5	
	peach	1	
	Japanese pear	1	
	pepper, sweet	0.5	
	persimmon	1	
	pumpkin	0.5	
	strawberries	1	
	tomato	0.5	
	watermelon	1	
	wheat	0.1	
Mexico	apples	0.1	ref. 1
	grapes	0.2	
	peas	0.1	
	pecan	0.1	
USA	apple	0.1	ref. 1
	cherry	1	
	grape	0.2	
	pear	0.1	
	pecan	0.1	
	cattle, fat	0.1	
	cattle, kidney	0.1	
	cattle, liver	0.1	
	cattle, meat by-products	0.01	
	cattle, meat	0.01	
	eggs	0.01	
	goats, fat	0.1	
	goats, kidney	0.1	
	goats, liver	0.1	
	goats, meat by-products	0.01	
	goats, meat	0.01	
	hog, fat	0.1	
	hog, kidney	0.1	
	hog, liver	0.1	
	hog, meat by-products	0.01	
	hog, meat	0.01	
	horse, fat	0.1	

Country	Crop	MRL, mg/kg	Ref.
	horse, kidney	0.1	
	horse, liver	0.1	
	horse, meat by-products	0.01	
	horse, meat	0.01	
	milk	0.003	
	poultry, fat	0.01	
	poultry, meat by-products	0.01	
	poultry, meat	0.01	
	sheep, fat	0.1	
	sheep, kidney	0.1	
	sheep, liver	0.1	
	sheep, meat by-products	0.01	
	sheep, meat	0.01	

[1] Applicable to Austria, Belgium, Denmark, Germany, Greece, Finland, France, Ireland, Italy, Luxembourg, The Netherlands, Portugal, Spain, Sweden and the UK
[2] To be set at 0.02* mg/kg (analytical limit of determination) unless further residue trials data are supplied

APPRAISAL

Fenarimol is a pyrimidin-5-ylbenzhydrol systemic fungicide, which is available in several formulations, the most important being emulsifiable concentrates, suspension concentrates, and wettable powders. It is registered for use on many crops world-wide. It was considered for the first time by the present Meeting.

Fenarimol is a crystalline solid of moderately low melting point and volatility. It has low solubility in water and is soluble in medium polarity solvents. The octanol/water partition coefficient indicates that the compound has the potential to accumulate to a moderate extent. It is photolabile in air and water and is not flammable, autoflammable, explosive or oxidizing.

In rats the major metabolic routes are oxidation of the carbinol, the chlorophenyl rings and the pyrimidine ring.

In goats a number of metabolites were formed, but they occurred at very low levels and would be unlikely to exceed 0.01 mg/kg following the feeding of crops (e.g apple pomace) which had been treated according to current GAP. The metabolites included *o*-chlorobenzoic acid and the methyl sulfone derivative of fenarimol, neither of which were identified as rat metabolites. Fenarimol was also detected in liver and kidney samples at low levels, and was the major component of the residue in pigs. In a poultry metabolism study the highest total residue occurred in the liver and kidneys. No identification of the residue was attempted although intakes by chickens from treated crops are likely to low (<0.1 ppm in the diet).

In apples and grapes fenarimol was degraded to numerous unidentified compounds at very low levels. These are likely to be photo-degradation products as they generally show very similar chromatographic characteristics. They do not occur in rats. The major component of the radioactive residue in apples, grapes and cucumbers was fenarimol. Six hours, 29 days and 49 days after spraying apples with [Æ-14C]fenarimol, the majority of the radioactive residue (81-92%) was associated with the peel.

A number of analytical methods were reported for a variety of substrates. Although these used different extraction and clean-up techniques, the determination in all was by GLC with an ECD, achieving LODs of 0.002-0.05 mg/kg.

Since the studies of metabolism by plants and livestock indicated that unchanged fenarimol was the major component of the residue, the Meeting concluded that the residue should be defined as fenarimol.

Residues in wine, grapes and cherries were found to be stable for at least 370, 370 and 104 days, respectively, following storage at *c.* -20°C. Additional data on the storage stability of residues were available for fortified peaches, tomatoes and melons, but were submitted too late for consideration by the Meeting: they will be evaluated by a future Meeting.

Important experimental details were missing from several of the residue trials. In cases where weather data, example chromatograms, crop variety or full details of the method of analysis for the particular trial were not provided the trials data were used, where applicable, to estimate maximum residue levels, since these omissions were not considered critical. However, where analytical recoveries associated with a trial were outside the range 70-120% the results were generally ignored. Similarly, if laboratory samples were stored frozen for more than 6 months or the duration and conditions of storage were unspecified the analytical results were not considered reliable. The exception to this was fruit crops for which data on the storage stability of residues were available. Finally in all cases a study report was considered necessary; a simple trial sheet was not considered to give sufficient information and such submissions as were not used in the estimation of maximum residue levels.

Apples. The results of a large number of trials were available from several countries around the world. The highest residues were found in trials according to Dutch GAP, but since the Dutch data were submitted only in summary form they were not used to estimate maximum residue levels. 16 Northern European trials reflected German GAP (0.0036 kg ai/hl, 21-day PHI) with residues of 0.02-0.21 mg/kg. A number of other German trials were reported but only summary sheets were submitted. US GAP was followed in eight trials in the USA, several of which were replicated, with residues 29-42 days after the final treatment of 0.002-0.059 mg/kg.

Eight trials according to GAP reported for Denmark, the UK and Ireland showed residues of 0.02-0.18 mg/kg. In further trials according to GAP in New Zealand, Brazil and Chile residues were 0.002-0.09 mg/kg. The Meeting estimated a maximum residue level of 0.3 mg/kg.

Pears. Four trials according to GAP were reported from the USA with residues of 0.01-0.04 mg/kg. Two trials were available with residues up to 0.13 mg/kg reflecting Italian and German GAP: the analytical recoveries associated with these trials were low at 63 and 67% respectively. The Meeting took into account the large number of trials on apples and the similar use patterns on the two crops, and estimated a maximum residue level of 0.3 mg/kg for pome fruits.

Peaches. Five peach trials in Spain and Italy according to Spanish GAP gave residues of 0.03-0.3 mg/kg at 7 days. In two of these trials the volume of spray per hectare was not clear and the results can therefore only be used as supplementary information. A further 1988 Spanish trial on apricots according to Spanish GAP for peaches with a residue of 0.36 mg/kg at 7 days provides support. The highest residues were from trials in which high water volumes were used but these complied with GAP. In a single Chilean nectarine trial according to Argentinian GAP residues were below the LOD at 2 days. No trials were available with results at the Japanese GAP PHI of one day. The Meeting estimated a maximum residue level of 0.5 mg/kg for peaches.

Cherries. Nine trials (3 with replicates) according to US GAP showed residues of 0.06-0.89 mg/kg at a 0- or 1-day PHI. It was recognised that no account was taken of the weights of the stones and the residues in the whole cherries would have been somewhat lower. The Meeting estimated a maximum residue level of 1 mg/kg for cherries.

Currants. Only 5 trials were available from The Netherlands and only one of these was according to GAP in Denmark, Ireland, The Netherlands or the UK. Furthermore, since the Dutch data were submitted only in summary form they could not be used. The Meeting concluded that there were insufficient data to estimate a maximum residue level for currants.

Gooseberries. Only one Dutch trial, reported in summary form only, was available: it complied with GAP reported for Ireland, The Netherlands and the UK. The Meeting concluded that there were insufficient data to estimate a maximum residue level.

Grapes. Residues in grapes treated according to GAP in the USA, Australia and France were generally low with residues of 0.003-0.06 mg/kg, 0.01-0.08 mg/kg and 0.02 mg/kg, respectively. A number of German trials were submitted of which six (2 with replicates) reflected German GAP (0.023 kg ai/ha, 35-day PHI). The residues were 0.01-0.15 mg/kg in samples taken 35 days after the final treatment. Seven of the German trials (two with replicates) which accorded with UK GAP (0.04 kg ai/ha, PHI 14 days) gave residues of 0.02-0.24 mg/kg in samples taken 14 days after the final treatment. There were no southern European trials at the highest GAP rate (0.06 kg ai/ha) or the shortest PHI (7 days). The Meeting estimated a maximum residue level of 0.3 mg/kg for grapes.

Strawberries. Residue trials data were available from Italy, Japan, Spain and The Netherlands. Three Italian trials were according to GAP (0.048 kg ai/hl, 7-day PHI), with residues of 0.12-0.18 mg/kg. Dutch trials reflecting GAP (0.084 kg ai/ha, treatment before flowering) showed residues of <0.01-0.02 mg/kg, but the data were submitted in summary form only and were therefore not considered further. Higher residues would result from Spanish GAP which has the shorter PHI of 3 days (0.0048 kg ai/hl) and which was represented by one trial with a residue of 0.25 mg/kg. Seven field trials were according to Japanese indoor GAP with a PHI of 1 day (0.03 kg ai/ha or 0.003 kg ai/hl). Residues in crops sampled one day after the final treatment were 0.04-0.56 mg/kg. The Meeting estimated a maximum residue level of 1 mg/kg for strawberries.

Raspberries. Only one residues trial was available from the UK and this was at a higher application rate than the GAP reported for Ireland and the UK. There were insufficient data to estimate a maximum residue level.

Bananas. Residue trials in Ecuador, Costa Rica and Honduras demonstrated that residues in unbagged bananas were generally higher than in bagged bananas. Six trials according to GAP in Honduras and Nicaragua (0.12 kg ai/ha, PHI 0 days) showed residues in unbagged bananas 0 or 1 day after the final treatment of <0.01-0.19 mg/kg. Six further trials at twice the registered application rate led to residues of 0.03-0.3 mg/kg in unbagged fruit. Residues were determined in the edible pulp. Although these were generally lower than those in the peel some were higher. The Meeting concluded that there was no consistent partition factor between the pulp and peel. It estimated a maximum residue level of 0.2 mg/kg.

Cucumbers. Only very limited data were available with one trial according to UK and Irish GAP (0.002 kg ai/hl, 2-day PHI) and one according to GAP in Uruguay. Residues were 0.03 mg/kg after 2 days and 0.003 mg/kg after 4 days respectively. The Meeting concluded that there were insufficient data to estimate a maximum residue level for cucumber.

Gherkins. Information on GAP gherkins in The Netherlands was reported as 0.0024 kg ai/hl, 6-day PHI, for both protected and field use. Two Dutch trials were reported with the high application concentration of 0.24 kg ai/hl but with the rate per hectare unspecified. However, since the data were submitted in summary form only they were unsuitable. The Meeting concluded that there were insufficient data to estimate a maximum residue level.

Melons (including cantaloupe) and watermelons. Data were available from two Spanish indoor trials but these were with a higher spray concentration than the reported Dutch GAP. Two trials were according to Brazilian GAP (0.024 kg ai/ha, 4-day PHI); the residues were 0.005 mg/kg in melons and "not detected" in watermelons.

Four French trials on melons were according to Greek GAP for "cucurbits" (0.024 kg ai/ha, 1-day PHI) with residues of <0.01 mg/kg in the pulp and up to 0.11 mg/kg in the peel of samples taken 2 days after the final treatment. However, no information was available on the weight ratio of the peel to the pulp. The manufacturer suggested a 30% peel to fruit weight ratio based on melon samples taken from other trials. Whilst the Meeting would not normally consider it appropriate to use an assumed weight ratio, this was considered an exceptional case since the residues were very low and calculations of the residues in whole melons from the trial with the highest residue level in the peel, based on an assumed peel:fruit weight ratio of 20-40%, would lead to values of 0.03-0.05 mg/kg if the residues in the pulp were at the limit of determination. Other trials were available which, although they did not correspond exactly to reported GAP (usually they were with exaggerated doses), indicated that residues were generally low. The Meeting estimated a maximum residue level of 0.05 mg/kg for melons. Since there were relatively few results the Meeting did not consider it appropriate to extrapolate this estimate to other cucurbits.

Pumpkins, courgettes and squashes. Only limited data were available, with no indoor trials according to Dutch indoor GAP.

Only one trial in Brazil, with a residue of 0.005 mg/kg, conformed to outdoor GAP in Argentina and Uruguay. Single Australian replicated trials on zucchini and pumpkins were according to Australian GAP for cucurbits. Residues were very low: 0.001-0.01 mg/kg three days after the final treatment. The Meeting concluded that there were insufficient data to estimate a maximum residue level for pumpkins, courgettes or squashes.

Tomatoes. Two indoor trials in The Netherlands were comparable to Danish GAP (0.036 kg ai/ha or 0.0048 kg ai/hl, 2-day PHI). Residues in both were 0.03 mg/kg at 2 days. Italian and Spanish outdoor GAP (0.0048 and 0.006 kg ai/hl, 7-day PHI) was reflected in two Italian trials and one Spanish trial with residues of 0.03, 0.03 and 0.05 mg/kg at 7 days. There were no outdoor trials according to Japanese GAP, which has a PHI of 1 day. Should submissions be made in the future, processing data will be required. There were insufficient data to estimate a maximum residue level.

Peppers. There were 6 trials in Italy and Spain according to Italian and Spanish GAP (the same as for tomatoes). The residues were 0.03 and 0.07 mg/kg in the Italian trials and 0.07, 0.08, 0.12 and 0.5 mg/kg in the Spanish trials, in samples taken 7 days after the final treatment. The Meeting estimated a maximum residue level of 0.5 mg/kg for peppers.

Aubergines. Only one Italian trial was available in which the residue was <0.01 mg/kg 15 days after treatment. This was insufficient to estimate a maximum residue level.

Beetroots and carrots. The only GAP reported for beetroots and carrots was the Dutch GAP for "vegetables" (0.036 kg ai/ha or 0.0024 kg ai/hl, 3-day PHI). Although one Netherlands trial was available for each of these crops, neither reflected GAP since samples were taken 27 days after treatment. No maximum residue level could be estimated.

Artichoke, Globe. Six Italian trials were considered to reflect Italian GAP (0.0048 kg ai/hl or 0.038 kg ai/ha, 7-day PHI) with residues of <0.01-0.06 mg/kg. Two of these trials (in 1979 with residues of <0.01 and 0.03 mg/kg) had a low associated analytical recovery (61%) and were therefore not considered reliable. A further Spanish trial gave a higher residue of 0.26 mg/kg at 7 days but a high volume of water (2,500 l/ha) was applied and the spray concentration (0.006 kg ai/hl) was higher than that registered in Italy. The Meeting estimated a maximum residue level of 0.1 mg/kg for globe artichokes.

Witloof chicory. Only one replicated trial in The Netherlands was available which complied with Dutch GAP for "vegetables". Residues were <0.01 mg/kg in samples taken 60 days after treatment. The Meeting concluded that there were insufficient data to estimate a maximum residue level for witloof chicory.

Pecans. Twelve trials were carried out in the USA of which four (one replicated) had application rates of 0.074-0.12 kg ai/ha, close to the registered rate in the USA (0.098 kg ai/ha). Residues in the kernels, to which the MRL applies, were <0.002 mg/kg at 35-153 days. In a further series of trials, residues in the kernels were all <0.002 mg/kg except in one trial with 0.02 mg/kg, at an exaggerated application rate (0.14-0.197 kg ai/ha). The residue of 0.02 mg/kg may have resulted from physical transfer from the shell. Recognising the need to establish MRLs at levels suitable for routine analysis by monitoring and enforcement laboratories, the Meeting estimated a maximum residue level of 0.02* mg/kg for pecans.

Hops. Four trials in Germany were all according to German GAP (0.06 kg ai/ha or 0.0015 kg ai/hl, 10-day PHI). The residues in dry hops harvested 10 days after the final treatment were 2.22-3.55 mg/kg, but in all the trials the hop samples were stored for 13 months before analysis. Brewing with these hops gave residues in the beer of <0.01 mg/kg. The results appeared very consistent and would suggest a maximum residue level of 5 mg/kg in dry hops, but in the absence of data confirming the stability of fenarimol in stored samples of a leafy crop the Meeting decided not to recommend an MRL: it was informed that a storage stability study on hops was now available.

Apple pomace. Processing data on apples indicated a concentration of residues from whole apples to dry pomace of 5-20-fold, with a median concentration factor of 14. Apple samples in several of the trials were "soak-washed" before analysis of the whole apples. The Meeting considered the data from these samples unsatisfactory. In the seven remaining trials with unwashed apples the median and mean concentration factors were 15 and 17 respectively. Although it was noted that the analytical recoveries from dry apple pomace were variable (68, 68, 76, 83, 108, 132 and 132%) the Meeting estimated a maximum residue level of 5 mg/kg for apple pomace, dry.

Dried grapes. Processing data on grapes indicated concentration factors for residues in whole grapes to those in raisins of 0.2-2.1. By applying the median concentration factor of 0.6 to the estimated maximum residue level of 0.3 mg/kg for grapes, the Meeting estimated a maximum residue level of 0.2 mg/kg for dried grapes.

Grape pomace, dry. Processing grapes to dry grape pomace increased the residues about 12-15 times, but as there were only two suitable results and residues in the grapes were low the Meeting could not establish a reliable concentration factor and therefore did not estimate a maximum residue level.

In a livestock feeding study beef cattle and pigs were fed for 28 days with fenarimol at various rates up to 1 ppm in the diet. At this dose residues of fenarimol in all tissue except liver were ≤0.01 mg/kg. Residues in the liver reached a maximum level of 0.03 mg/kg in pigs and 0.05 mg/kg in cattle. At rates of 0.1 and 0.3 ppm all tissue residues were <0.01 mg/kg.

Livestock will obtain fenarimol from wheat grain and straw, peas and pea straw, and fruit pomace. Of these items sufficient data on residues were available only for dry apple pomace (estimated maximum residue level 5 mg/kg). Dairy and beef cattle consume a maximum of 30% of their dietary dry matter as fruit pomace, whereas it is not generally fed to pigs. The maximum intake of fenarimol by beef cattle from fruit pomace would therefore be approximately 1 ppm in the diet. The Meeting recognized the need to establish MRLs at levels suitable for routine analysis by monitoring and enforcement laboratories, and estimated maximum residue levels of 0.02* mg/kg for cattle meat and kidney and 0.05 mg/kg for cattle liver.

There were insufficient data on pig feed items to estimate a maximum residue level for the meat or edible offal of pigs.

Although data on the environmental fate of fenarimol in soil were submitted to the Environmental Core Assessment Group at the present Meeting they were not, as would normally be expected, submitted for the consideration of the FAO Panel. The manufacturer agreed to submit the data to the FAO, for future consideration by the FAO Panel, as soon as possible. The Meeting concluded that in these circumstances temporary MRLs should be recommended, with a requirement for the studies on environmental fate.

RECOMMENDATIONS

The Meeting estimated the temporary maximum residue levels shown below, which are recommended for use as TMRLs.

Definition of the residue: fenarimol

CNN	Commodity	Recommended MRL, mg/kg	PHI on which based, days
AB 0266	Apple pomace, dry	5T	-
VS 620	Artichoke, Globe	0.1T	7
FI 327	Banana	0.2T	0
MM 812	Cattle meat	0.02*T	-
MO 1280	Cattle kidney	0.02*T	-
MO 1281	Cattle liver	0.05T	-
FS 13	Cherry	1T	0
DF 269	Dried grape	0.1T	-
FB 269	Grape	0.3T	14
VC 46	Melons, except Watermelon	0.05T	1
FS 247	Peach	0.5T	7
TN 672	Pecan	0.02*T	30
VO 445	Peppers, Sweet	0.5T	7
FP 9	Pome fruits	0.3T	14-28
FB 275	Strawberry	1T	1

FURTHER WORK OR INFORMATION

Required (by 1996)

Data on the environmental fate of fenarimol in soil.

Desirable

1. Full details of the methods of analysis used in all the residue studies where this information was not given. Validation of the methods of analysis for which validation data were not submitted.

2. A study to assess the likely residues in relevant succeeding or rotational crops or an explanation of why residues would not be expected.

3. Information on the melting point, octanol/water partition coefficient, solubility and specific gravity of pure fenarimol.

4. Submission of the study reports supporting the trials on apples, gooseberries, currants, gherkins and strawberries conducted in The Netherlands.

REFERENCES

Althaus, W.A. 1982a. ^{14}C Fenarimol Chicken Tissue Residue Study. Sept ABC-0186. Ref. NA 06.

Althaus, W.A. 1982b. ^{14}C Fenarimol Chicken Egg Residue Study. Sept ABC-0147. Ref. NA 07.

Althaus, W.A. 1984a. A Comparative Apple Residue Study Conducted with Carbinol-labelled and mixed-labelled ^{14}C Fenarimol. Mar ABC-0199. Ref. L 02.

Althaus, W.A. 1984b. ^{14}C Fenarimol Grape Residue Study. Apr ABC-0237, ABC-0239. Ref. L 03.

Althaus, W.A. 1985a. Characterization and Identification of Radioactivity in Urine and Feces of Wistar Rates given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0310. Ref. H 10.

Althaus, W.A. 1985b. Characterization and Identification of Radioactivity in Blood, Liver, and Kidney of Wistar Rats given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0321. Ref. H 11.

Althaus, W.A. 1986. ^{14}C Fenarimol Residue Study in Cucumbers. Oct ABC-0307. Ref. L 08.

Althaus, W.A. and Bewley, G.W. 1978a. ^{14}C Fenarimol Apple Residue Study Jan Ref. L 09.

Althaus, W.A. and Bewley, G.W. 1978b. Separation and Identification of Degradation Products formed from ^{14}C Fenarimol Applied to Apples. Jan Ref. L 01.

Althaus, W.A. *et al.* 1984. ^{14}C Fenarimol Swine Tissue Residue Study. Apr ABC-0202. Ref. NA 09.

Arcas, J.B. 1986. Analises de Residuos de Fenarimol em Frutos e Cucurbitaceas Ref. NB 29.

Arnold, M. 1995. Dow Elanco Europe. Spanish residue trials data for apricots, peaches, melons, artichoke, peppers and strawberry submitted with letter dated 17th July Unpublished. Ref. 13.

Arnold, M. 1995. Dow Elanco Europe. Personal Communication. 16th August Ref. 10.

Butcher, S.M. 1992. Determination of Fenarimol Residues in Beer and Spent Yeast. Jan ERC91-10. Ref. OR 21.

Butcher, S.M. 1993. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12ec (EAF 457), Spain Aug 1994 GHE-P-3653. Ref. NE 08.

Butcher, S.M. 1994a. Determination of Residues of Fenarimol in Tomatoes, Peaches and Melons ERC 94.3 Aug Ref. OR 24.

Butcher, S.M. 1994b. The Stability of Fenarimol in Fortified Grapes and Wine stored under Frozen Conditions GHE-P-3741 Aug Ref. NH 10.

Butcher, S.M. 1995a. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12SC (EAF 383), Netherlands Jan 1995. GHE-P-4008. Ref. NE 11.

Butcher, S.M. 1995b. Residues in Melons Spain Jan 1995 GHE-P-4011. Ref. NB 31.

Butcher, S.M. 1995c. Residues of Fenarimol in Tomatoes - Greece Jan 1995. GHE-P-4012. Ref. NE 12.

Butcher, S.M. 1995d. Residues in Melons Italy Jan 1995 GHE-P-4013. Ref. NB 32.

Butcher, S.M. 1995e. Peaches Italy Jan GHE-P-4014. Ref. NG 10.

Butcher, S.M. 1995f. Peaches France Jan GHE-P-4062. Ref. NG 11.

Butcher, S.M. 1995g. The stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditons. GHE-P-4318. Ref. NG 12.

Butcher, S.M. 1995h. Residues of Fenarimol in Globe Artichokes at Intervals following Multiple Applications of RUBIGAN 12 SC (EAF383), Italy GHE-P4010 Jan 1995. Ref. NI 05.

Butcher, S.M. and Long, T.J. 1993. Determination of Residues of Fenarimol in Grape Must, Wine and Grapes. ERC93-6 Jul Ref. OR 22.

Butcher, S.M. and Perkins, J. 1991. Residues of fenarimol in Hops and related fractions from the brewing process following application of Drawisan 6WP (EAF 219) - Germany 1990. GHE-P-2517 Oct Ref. NJ 01.

Butcher, S.M. and Perkins, J.M. 1992. Determination of Fenarimol Residues in Fresh, Dried and Spent Hops. ERC91-8 Jan Ref. OR 20.

Butcher, S.M. and Wood, S. 1994a. Residues of Fenarimol in Grapes at Intervals following Application of TRANSFLO (EAF 383), France - GHE-P-3627 Jun 1994. Ref. NH 04.

Butcher, S.M. and Wood, S. 1994b. Residues of Fenarimol in Peaches at intervals following Application of RUBIGAN 12sc (EAF383), Italy - GHE-P-3626 Jun 1994. Ref. NG 08.

Butcher, S.M. and Wood, S. 1994c. Residues of Fenarimol in Grapes, Grape Must and Wine following Application of Rubigan 12 SC (EAF 383) to Grape Vines Germany GHE-P-3655 Aug 1994. Ref. NH 11.

Butcher, S.M. and Wood, S. 1994d. Residues of Fenarimol in Peaches at intevals following Application of RUBIGAN 4 (EAF 216), - Southern France GHE-P-3652 Aug 1994. Ref. NG 07.

Catta-Preta, R.F. and Matos, J.C. 1992 Residues of Fenarimol and its Major Metabolites in Bananas following Multiple treatments with Rubigan Ec Fungicide - Costa Rica, Honduras and Ecuador, April 1993 GHB-P 151. Ref. NL 02.

Catta-Preta, R.F. and Matos, J.C. 1993. Determination of

Residues of Fenarimol, Compound 212746 and 210302 in Banana Whole Fruit and Pulp BRC 92.2 March Ref. R 28.

Coleman, I. 1995. Commonwealth Department of Primary Industries and Energy, Australia. Personal Communication. 12th April Ref. 2.

Cowlyn, T.C. 1992. Fenarimol (pure): Determination of Physico-Chemical Properties (Vapour Pressure) Sept 93/DES080/0411. Ref. A 21.

Cowlyn, T.C. 1992. Fenarimol (technical): Determination of Physico-Chemical Properties (Flammability, Auto-flammability, Explosive and Oxidising Properties) Oct 92/DES081/0866. Ref. A 22.

Crossley, S.J. 1994. Pesticides Safety Directorate, UK. Personal Communication. 31st November Ref. 9.

Day, E.W. 1976. Solubility of Fenarimol in Organic Solvents. Sept FLP V-131. Ref. A 09.
Day, E.W. 1981. Fenarimol Residue Data on Apples from Canada May Ref. NF 27.

Day, E.W. 1981. Fenarimol Residues in Apples from New Zealand Mar NZ75-19, 1988 NZ78-2, NZ80-5, NZ80-6. Ref. NF 29.

Day, E.W. 1981. Fenarimol Residues in Apples from Chile May T2R-230. Ref. NF 28.

Day, E.W. 1983. Fenarimol Residue Data on Grapes and Grape Products from Experiment conducted in the United States in March 1984 I-EWD-84-03. Ref. NH 17.

Day, E.W. 1985. Fenarimol Technical Product Chemistry Data. Ref. A 08.

Day, E.W. 1987. Fenarimol Residue Data on Pears March EWD8640. Ref. NF 33.

Day, E.W. 1993. Reasonable Grounds in Support of the Petition for the Establishment of A Tolerance for Fenarimol and its Metabolites in or on Bananas. Aug ECL93073. Ref. NL

Day, E.W. Undated. Preliminary Photochemical Studies with the Fungicide EL-222. Ref. K 26.

Day, E.W and Saunders, D.G. 1987. Fenarimol Residue Studies in Cherries AAC8713 Feb 1988. Ref. NG 04.

Day, E.W. and Saunders, D.G. 1988. Storage Stability of Fenarimol in Cherries EWD8803 Feb Ref. NG 06.

Day, E.W. Jr. and Saunders D.G. 1988. Storage Stability of Fenarimol and its Metabolites in Grapes and Grape Products. EWD8802 Apr Ref. NH 07.

Day, E.W. and West, S.D. 1988. Fenarimol Residue Studies in Apples Nov 1988. AAC8819. Ref. NF 31.

Day, E.W. and West, S.D. 1988 Fenarimol Residue Trials in Grapes AAC8818 Dec 1988. Ref. NH 20.

Day, E.W. and West, S.D. 1989. Fenarimol Residue Studies in Cherries, Aug 1989 AAC8903. Ref. NG 05.

Day, E.W. *et al.* 1984. Physical and Chemical Characteristics of Technical Fenarimol Nov EWD8450. Ref. A 14.

Decker, O.D. 1983. Fenarimol Residues on Pecans when Rubigan 1EC or Rubigan 1AS is Foliar applied to Pecan Trees on Disease Control March I-ODD-82-02. Ref. NM 01.

Decker, O.D. 1984. Fenarimol Residues on Pecans when Rubigan is Foliar applied to Pecan Trees for Disease Control Feb I-ODD-84-01. Ref. NM 02.

Decker, O.D. and Day, E.W. 1981. Fenarimol Residue Data on Apples and Apple Products from Experiments conducted in the United States in and 1982. Mar 1983. I-ODD-83-06. Ref. NF 18.

Dow Elanco Ltd. 1976. Determination of EL-222 in Agricultural Crops and Soils by Gas-Liquid Chromatography Std An.Method No.86 Sep Ref. OR 10.

Dow Elanco Ltd. 1976. Residue Study - Cucumber - Austria A76-106. Ref. NB 01.

Dow Elanco Ltd. 1976. Residue Study - Melon- France F76-04. Ref. NB 02.

Dow Elanco Ltd. 1976. Residue Study-Cucumber-Italy 176-33. Ref. NB 03.

Dow Elanco Ltd. 1976. Residue Study - Cucumber - UK FG76-016. Ref. NB 04.

Dow Elanco Ltd. 1977. Determination of Fenarimol In Agricultural Crops (Other than Cereals) by Gas-Liquid Chromatography Nov Std.An.Method No.97. Ref. OR 11.

Dow Elanco Ltd. 1977. Residue Study - Cucumber - Italy 177-234. Ref. NB 08.

Dow Elanco Ltd. 1977. Residue Study - Cucumber - Italy 177-235. Ref. NB 09.

Dow Elanco Ltd. 1977. Residue Study - Squash - Italy 177-236. Ref. NB 10.

Dow Elanco Ltd. 1977. Residue Study - Cantaloupe - Italy 177-251. Ref. NB 11.

Dow Elanco Ltd. 1977. Residue Study - Watermelon - Italy 177-253. Ref. NB 12.

Dow Elanco Ltd. 1977. Residue Study - Peppers - Spain E77-129. Ref. NE 02.

Dow Elanco Ltd. 1977. Residue Study - Peach - Italy 177-212. Ref. NG 01.

Dow Elanco Ltd. 1977. Residue Study - Peach 177-213. Ref. NG 02.

Dow Elanco Ltd. 1977. Residue Study - Peach - Italy 177-214. Ref. NG 03.

Dow Elanco Ltd. 1977. Residue Study - Grape A77-121. Ref. NH 05.

Dow Elanco Ltd. 1977. Residue Study - Grape A77-122. Ref. NH 06.

Dow Elanco Ltd. 1977. Residue Study - Grape 177-225. Ref. NH 09.

Dow Elanco Ltd. 1978. Residue Study - Pears - Germany D78-312. Ref. NF 03.

Dow Elanco Ltd. 1978. Residue Study - Apples - Germany D78-311. Ref. NF 08.

Dow Elanco Ltd. 1979. Residue Study - Artichoke - Italy 179-251. Ref. N1 02.

Dow Elanco Ltd. 1979. Residue Study - Strawberry - Italy 179-252. Ref. NC 11.

Dow Elanco Ltd. 1979. Residue Study - Strawberry - Italy 179-253. Ref. NC 12.

Dow Elanco Ltd. 1979. Residue Study - Tomatoes - Italy 179-251. Ref. NE 03.

Dow Elanco Ltd. 1979. Residue Study - Peppers - Israel ISL79-2. Ref. NE 04.

Dow Elanco Ltd. 1979 Residue Study - Pepper - Italy 179-250. Ref. NE 05.

Dow Elanco Ltd. 1979 Residue Study - Pepper - Italy 179-251. Ref. NE 06.

Dow Elanco Ltd. 1979. Residue Study - Tomatoes - Italy 179-250. Ref. NE 07.

Dow Elanco Ltd. 1979. Residue Study - Artichoke - Italy 179-250. Ref. NI 01.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-729. Ref. NB 20.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-730. Ref. NB 21.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-730A. Ref. NB 22.

Dow Elanco Ltd. 1980. Residue Study - Melons - France F80-735. Ref. NB 23.

Dow Elanco Ltd. 1981/2. Residues Studies - Grapes - Germany and France Apr 1983. Ref. NH 12.

Dow Elanco Ltd. 1981. Residue Studies-Apples Germany and UK/Apr 1983. D81-302, D81-350, D81-351, D81-353, FF81-002. Ref. NF 20.

Dow Elanco Ltd. 1981. Residue Study - Cucumbers - Italy 181-255. Ref. NB 15.

Dow Elanco Ltd. 1981. Residue Study - Cantaloup - Italy 181-256. Ref. NB 24.

Dow Elanco Ltd. 1981. Residue Study - Squash - Italy 181-254. Ref. NB 26.

Dow Elanco Ltd. 1981. Residue Study - Artichokes - Italy 181-251. Ref. NB 28.

Dow Elanco Ltd. 1981. Residue Study - Tomatoes - Italy 181-258. Ref. NE 09.

Dow Elanco Ltd. 1981. Residue Study - Pepper - Italy 181-259. Ref. NE 10.

Dow Elanco Ltd. 1981. Residue Study - Pears - Italy 181-211. Ref. NF 06.

Dow Elanco Ltd. 1982. Residue Studies - Apples Germany Apr 1983. D82-301, D82-302, D82-303, D82-304, D82-305, D82-307. Ref. NF 21.

Dow Elanco Ltd. 1987. Submission to T.C.A.C - Rubigan Data Supporting Reduction in Withholding Period in Grapes (contains Australian Residue data) July Ref. NH 23.

Dow Elanco Ltd. 1993. Residues in Nectarines in Chile, Gonzalez, R.H Degradacion de Residous de Rubigan en Nectarinos Y Fijacion de Carencias Preliminares Chile Ref. NG 09.

Dow Elanco Ltd. 1994. Europe. Italian GAP for peaches. 17th July Unpublished. Ref. 12.

Dow Elanco Ltd. 1995. Summary of Data, Fenarimol JMPR, March Unpublished. Ref. 1.

Dow Elanco Ltd. 1995. Product Labels, Fenarimol JMPR, March Unpublished. Ref. 4.

Dow Elanco Ltd. 1995. Residues of fenarimol in fresh and processed grapes after treating Cabernet Sauvignon and Sultana grapevines with Rubigan 120 EC®. March. Ref. NH 24.

Dow Elanco Ltd. Undated. Residue Study - Grapes AAC8714. Ref. NH 01.

Dow Elanco Ltd. Undated. Residues Study - Grapes EWD8703. Ref. NH 02.

Dow Elanco Ltd. Undated. Application for clearance of RUBIGAN systemic Fungicide to the Technical Committee on Agricultural Chemicals Section E-Residues (Australian Data Summary). Ref. NB 30.

Dow Elanco Ltd. Undated. Rate of Hydrolysis of EL-222. Ref. K 25.

European Union. 1994. Council Directives 94/29/EEC and 94/30/EEC. July Ref. 3.

Frank, R. 1977. Fenarimol Residues in Whole Apple Fruit

(Canada) May T2R-233. Ref. NF 25.

Frank, R. 1978. Fenarimol Residues in Whole Apple Fruit (Canada) July T2R-198. Ref. NF 26.

Germany. 1994. Submission made by the Federal Biological Research Centre for Agriculture and Forestry, July 1994. Unpublished. Ref. 8.

Goebel, G.V. 1985a. Characterization of Radioacativity in bile from rats dosed orally with ^{14}C Fenarimol. May ABC-0312. Ref. H 04.

Goebel, G.V. 1985b. Isolation and Identification of "Metabolite Complex" from 14C Fenarimol-Treated Grapes Mar ABC-0316. Ref. L 04.

Griggs, R.D and Decker, O.D. 1981. Determination of Fenarimol in Agricultural Crops and Soil Jan AM-AACA-R039-AA-755. Ref. OR 01A.

Griggs, R.D. and Decker, O.D. 1985. Determination of Fenarimol in Agricultural Crops and Soil Jan AM-AA-CA-RO39-AB-755. Ref. OR 01B.

Hudson, J.L. 1987. Fenarimol Technical, Bulk Density, Part 158 Product Chemistry Requirement. Nov T2R908703. Ref. A 10.

Ishikura, H. 1991. Residues of Fenarimol in Pulp, Peel and Whole Bananas Following application of Rubigan 12EC Fungicide in the Philippines - July 1991. GHF-P -1126. Ref. NL 03.

Koons, J.R. *et al*. 1984. Determination of Tissue Residues in Swine and Beef Cattle Fed Diets Containing Fenarimol. Mar S-AAC-83-04. Ref. NA 10.

Loh, A. 1976. n-Octanol-To-Water Partition Coefficient of Fenarimol. Dec EWD 8742. Ref. A 17.
Longhurst, C. 1985. Residues of Fenarimol in Raspberries following Foliar Applications of RUBIGAN Sept FF84-006. Ref. ND 01.

Lunn, D.W. 1995. Ministry of Agriculture and Fisheries, New Zealand. Personal Communication. 25th May Ref. 5.

Mason, R. 1995. Pesticides Safety Division, MAFF, UK. Personal Communication. 9th September Ref. 11.

McCorquodale, G.Y. and Prout, M.S. 1994. The disposition of [^{14}C]-fenarimol in the lactating goat. DowElanco Ltd., Report No. 10422. Ref. H 17.

Mosier, J.W. and Saunders, D.G. 1976. Photochemical Studies with Fenarimol. Aug Ref. K 28.

Netherlands, Ministry of Welfare, Health and Cultural Affairs, 1994. Netherlands. Personal Communication. September 1994. Ref. 6.

Pastor Talledo, C. 1994. Direccion de hygiene, Alimentarius y Control de Zoonosis, Peru. Personal communication. 23th November Ref. 7.

Rainey, D.P. 1987. Supplementary Information on Metabolism of ^{14}C Fenarimol in Grapes. Nov ABC-0239S. Ref. L 05.

Dow Elanco Ltd. 1988. Rubigan 12 WP/Strawberry Crop Residue Study: Japan 1984 and 1988 Studies 1994. June 1988 T2R-077. Ref. NC 16.

Trevallyn-Jones, J. 1984. Further Submission to T.C.A.C. - Withholding Period in Grapes treated with RUBIGAN (contains Australian Dow Elanco Ltd. Residue data) July Ref. NH 22.

Turner, L.G. 1992. [where has the DL come from?] Dow Elanco 1982. Ltd. Residue Method Development Report for Fenarimol and its Metabolites in Whole Bananas and Banana Pulp. GH-C-2840 Aug

Yordy, D.W. and Turner, L.G. Determination of Fenarimol In Meat, Milk and Eggs. AM-AA-CA-RO72-AA-755 Sep Ref. OR 27. Ref. OR 19.

NUMERICAL REFERENCES

1. Dow Elanco Ltd. Summary of Data, Fenarimol JMPR, March 1995. Unpublished.

2. Coleman, I. Commonwealth Department of Primary Industries and Energy, Australia. Personal Communication. 12th April 1995.

3. European Union Council Directives 94/29/EEC and 94/30/EEC. July 1994.

4. Dow Elanco Ltd. Product Labels, Fenarimol JMPR, March 1995. Unpublished.

5. Lunn, D.W. Ministry of Agriculture and Fisheries, New Zealand. Personal Communication. 25th May 1995.

6. Netherlands, 1994. Ministry of Welfare, Health and Cultural Affairs, Netherlands. Personal Communication. September 1994.

7. Pastor Talledo, C. 1994. Direccion de hygiene, Alimentarius y Control de Zoonosis, Peru. Personal communication. 23th November 1994.

8. Germany, 1994. Submission made by the Federal Biological Research Centre for Agriculture and Forestry, July 1994. Unpublished.

9. Crossley, S.J. Pesticides Safety Directorate, UK. Personal Communication. 31st November 1994.

10. Arnold, M. Dow Elanco Europe. Personal Communication. 16th August 1995.

11. Mason. R. Pesticides Safety Division, MAFF, UK. Personal Communication. 9th September 1995.

12. Dow Elanco Europe. Italian GAP for peaches. 17th July 1994. Unpublished.

13. Arnold, M. Dow Elanco Europe. Spanish residue trials data for apricots, peaches, melons, artichoke, peppers and strawberry submitted with letter dated 17th July 1995. Unpublished.

A 03. Decker, O.D. Solubility of Fenarimol in Water Oct 1987 ODD8711.

A 08. Day, E.W. Fenarimol Technical Product Chemistry Data. 1985.

A 09. Day, E.W. Solubility of Fenarimol in Organic Solvents. Sept 1976 FLP V-131.

A 10. Hudson, J.L. Fenarimol Technical, Bulk Density, Part 158 Product Chemistry Requirement. Nov 1987 T2R908703.

A 14. Day, E.W. *et al*. Physical and Chemical Characteristics of Technical Fenarimol Nov 1984 EWD8450.

A 17. Loh, A. n-Octanol-To-Water Partition Coefficient of Fenarimol. Dec 1976. EWD 8742.

A 21. Cowlyn, T.C. Fenarimol (pure): Determination of Physico-Chemical Properties (Vapour Pressure) Sept 1992 93/DES080/0411.

A 22. Cowlyn, T.C. Fenarimol (technical): Determination of Physico-Chemical Properties (Flammability, Auto-flammability, Explosive and Oxidising Properties) Oct 1992 92/DES081/0866.

H 04. Goebel, G.V. 1985a. Characterization of Radioacativity in bile from rats dosed orally with ^{14}C Fenarimol. May ABC-0312.

H 10. Althaus, W.A. 1985a. Characterization and Identification of Radioactivity in Urine and Feces of Wistar Rates given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0310.

H 11. Althaus, W.A. 1985b. Characterization and Identification of Radioactivity in Blood, Liver, and Kidney of Wistar Rats given single oral doses of mixed-labelled ^{14}C Fenarimol. Dec ABC-0321.

H 17. McCorquodale, G.Y. and Prout, M.S. 1994. The disposition of [^{14}C]-fenarimol in the lactating goat. DowElanco Ltd., Report No. 10422.

K 25. Dow Elanco Ltd. Rate of Hydrolysis of EL-222.

K 26. Day, E.W. Preliminary Photochemical Studies with the Fungicide EL-222.

K 28. Mosier, J.W. and Saunders, D.G. Photochemical Studies with Fenarimol. Aug 1976.

L 01. Althaus, W.A. Bewley, G.W. Separation and Identification of Degradation Products formed from ^{14}C Fenarimol Applied to Apples. Jan 1978b.

L 02. Althaus, W.A. A Comparative Apple Residue Study Conducted with Carbinol-labelled and mixed-labelled ^{14}C Fenarimol. Mar 1984b ABC-0199.

L 03. Althaus, W.A. ^{14}C Fenarimol Grape Residue Study. Apr 1984 ABC-0237, ABC-0239.

L 04. Goebel, G.V. Isolation and Identification of "Metabolite Complex" from ^{14}C Fenarimol-Treated Grapes Mar 1985 ABC-0316.

L 05. Rainey, D.P. Supplementary Information on Metabolism of ^{14}C Fenarimol in Grapes. Nov 1987 ABC-0239S.

L 08. Althaus, W.A. ^{14}C Fenarimol Residue Study in Cucumbers. Oct 1986. ABC-0307.

L 09. Althaus, W.A. Bewley, G.W14C Fenarimol Apple Residue Study Jan 1978a.

N1 02. Dow Elanco Ltd. Residue Study - Artichoke - Italy 1979 179-251.

NA 06. Althaus, W.A. ^{14}C Fenarimol Chicken Tissue Residue Study. Sept 1982. ABC-0186.

NA 07. Althaus, W.A.^{14}C Fenarimol Chicken Egg Residue Study. Sept 1982 ABC-0147.

NA 09. Althaus, W.A. *et al*. ^{14}C Fenarimol Swine Tissue Residue Study. Apr 1984a. ABC-0202.

NA 10. Koons, J.R. *et al*. Determination of Tissue Residues in Swine and Beef Cattle Fed Diets Containing Fenarimol. Mar 1984 S-AAC-83-04.

NB 01. Dow Elanco Ltd. Residue Study - Cucumber - Austria 1976 A76-106.

NB 02. Dow Elanco Ltd. Residue Study - Melon- France 1976 F76-04.

NB 03. Dow Elanco Ltd. Residue Study-Cucumber-Italy 1976 176-33.

NB 04. Dow Elanco Ltd. Residue Study - Cucumber - UK 1976 FG76-016.

NB 08. Dow Elanco Ltd. Residue Study - Cucumber - Italy 1977 177-234.

NB 09. Dow Elanco Ltd. Residue Study - Cucumber - Italy 1977 177-235.

NB 10. Dow Elanco Ltd. Residue Study - Squash - Italy 1977 177-236.

NB 11. Dow Elanco Ltd. Residue Study - Cantaloupe - Italy 1977 177-251.

NB 12. Dow Elanco Ltd. Residue Study - Watermelon - Italy 1977 177-253.

NB 15. Dow Elanco Ltd. Residue Study - Cucumbers - Italy 1981 181-255.

NB 20. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-729.

NB 21. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-730.

NB 22. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-730A.

NB 23. Dow Elanco Ltd. Residue Study - Melons - France 1980 F80-735.

NB 24. Dow Elanco Ltd. Residue Study - Cantaloup - Italy 1981 181-256.

NB 26. Dow Elanco Ltd. Residue Study - Squash - Italy 1981 181-254.

NB 28. Dow Elanco Ltd. Residue Study - Artichokes - Italy 1981 181-251.

NB 29. Arcas, J.B. Analises de Residuos de Fenarimol em Frutos e Cucurbitaceas 1986.

NB 30. Dow Elanco Ltd. Application for clearance of RUBIGAN systemic Fungicide to the Technical Committee on Agricultural Chemicals Section E-Residues (Australian Data Summary). Undated.

NB 30. Application for clearance of RUBIGAN systemic Fungicide to the Technical Committee on Agricultural Chemicals Section E - Residues, 1979.

NB 31. Butcher, S. Residues in Melons Spain 1994 Jan 1995 GHE-P-4011.

NB 32. Butcher, S. Residues in Melons Italy 1994 Jan 1995 GHE-P-4013.

NC 11. Dow Elanco Ltd. Residue Study - Strawberry - Italy 1979 179-252.

NC 12. Dow Elanco Ltd. Residue Study - Strawberry - Italy 1979 179-253.

NC 16. Rubigan 12 WP/Strawberry Crop Dow Elanco Ltd. Residue Study: Japan 1984 and 1988 Studies June 1988 T2R-077.

ND 01. Longhurst, C Residues of Fenarimol in Raspberries following Foliar Applications of RUBIGAN Sept 1985 FF84-006.

NE 02. Dow Elanco Ltd. Residue Study - Peppers - Spain 1977 E77-129.

NE 03. Dow Elanco Ltd. Residue Study - Tomatoes - Italy 1979 179-251.

NE 04. Dow Elanco Ltd. Residue Study - Peppers - Israel 1979 ISL79-2.

NE 05. Dow Elanco Ltd. Residue Study - Pepper - Italy 1979 179-250.

NE 06. Dow Elanco Ltd. Residue Study - Pepper - Italy 1979 179-251.

NE 07. Dow Elanco Ltd. Residue Study - Tomatoes - Italy 1979 179-250.

NE 08. Butcher, S.M. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12ec (EAF 457), Spain 1993 Aug 1994 GHE-P-3653.

NE 09. Dow Elanco Ltd. Residue Study - Tomatoes - Italy 1981 181-258.

NE 10. Dow Elanco Ltd. Residue Study - Pepper - Italy 1981 181-259.

NE 11. Butcher, S.M. Residues of Fenarimol in Tomatoes at Intervals Following Application of RUBIGAN 12SC (EAF 383), Netherlands 1994 Jan 1995
. GHE-P-4008.

NE 12. Butcher, S.M. Residues of Fenarimol in Tomatoes - Greece 1994 Jan 1995
. GHE-P-4012.

NF 03. Dow Elanco Ltd. Residue Study - Pears - Germany 1978 D78-312.

NF 06. Dow Elanco Ltd. Residue Study - Pears - Italy 1981 181-211.

NF 08. Dow Elanco Ltd. Residue Study - Apples - Germany 1978 D78-311.

NF 18. Decker, O.D. and Day, E.W. Fenarimol Residue Data on Apples and Apple Products from Experiments conducted in the United States in 1981 and 1982. Mar 1983. I-ODD-83-06.

NF 20. Dow Elanco Ltd. Residue Studies-Apples Germany and UK/1981 Apr 1983
. D81-302, D81-350, D81-351, D81-353, FF81-002.

NF 21. Dow Elanco Ltd. Residue Studies - Apples Germany 1982 Apr 1983. D82-301, D82-302, D82-303, D82-304, D82-305, D82-307.

NF 25. Frank, R. Fenarimol Residues in Whole Apple Fruit (Canada) May 1977 T2R-233.

NF 26. Frank, R. Fenarimol Residues in Whole Apple Fruit (Canada) July 1978 T2R-198.

NF 27. Day, E.W. Fenarimol Residue Data on Apples from Canada May 1981.

NF 28. Day, E.W. Fenarimol Residues in Apples from Chile May 1981 T2R-230.

NF 29. Day, E.W. Fenarimol Residues in Apples from New Zealand Mar 1981. NZ75-19, NZ78-2, NZ80-5, NZ80-6.

NF 31. Day, E.W. West, S.D 1988 Fenarimol Residue

Studies in Apples Nov 1988. AAC8819.

NF 33. Day, E.W. Fenarimol Residue Data on Pears March 1987 EWD8640.

NG 01. Dow Elanco Ltd. Residue Study - Peach - Italy 1977 177-212.

NG 02. Dow Elanco Ltd. Residue Study - Peach 1977 177-213.

NG 03. Dow Elanco Ltd. Residue Study - Peach - Italy 1977 177-214.

NG 04. Day, E.W and Saunders, D.G. 1987 Fenarimol Residue Studies in Cherries AAC8713 Feb 1988.

NG 05. Day, E.W. and West, S.D. 1989 Fenarimol Residue Studies in Cherries, Aug 1989 AAC8903.

NG 06. Day, E.W. and Saunders, D.G Storage Stability of Fenarimol in Cherries EWD8803 Feb 1988.

NG 07. Butcher, S. and Wood, S. Residues of Fenarimol in Peaches at intevals following Application of RUBIGAN 4 (EAF 216), - Southern France 1993 GHE-P-3652 Aug 1994.

NG 08. Butcher, S. and Wood, S. Residues of Fenarimol in Peaches at intervals following Application of RUBIGAN 12sc (EAF383), Italy - 1993 GHE-P-3626 Jun 1994.

NG 09. Dow Elanco Ltd. Residues in Nectarines in Chile, Gonzalez, R.H Degradacion de Residous de Rubigan en Nectarinos Y Fijacion de Carencias Preliminares Chile 1993.

NG 10. Butcher, S. Peaches Italy Jan 1995 GHE-P-4014.

NG 11. Butcher, S. Peaches France Jan 1995 GHE-P-4062.

NG 12. Butcher, S. The stability of fenarimol in fortified peaches, tomatoes and melons under frozen storage conditons. GHE-P-4318.

NH 01. Dow Elanco Ltd. Residue Study - Grapes AAC8714.

NH 02. Dow Elanco Ltd. Residues Study - Grapes EWD8703.

NH 04. Butcher, S. and Wood, S. Residues of Fenarimol in Grapes at Intervals following Application of TRANSFLO (EAF 383), France - 1993 GHE-P-3627 Jun 1994.

NH 05. Dow Elanco Ltd. Residue Study - Grape 1977 A77-121.

NH 06. Dow Elanco Ltd. Residue Study - Grape 1977 A77-122.

NH 07. Day, E.W. Jr. and Saunders D.G. Storage Stability of fenarimol and its Metabolites in Grapes and Grape Products. EWD8802 Apr 1988.

NH 09. Dow Elanco Ltd. Residue Study - Grape 1977 177-225.

NH 10. Butcher, S. The Stability of Fenarimol in Fortified Grapes and Wine stored under Frozen Conditions GHE-P-3741 Aug 1994.

NH 11. Butcher, S. and Wood, S. Residues of Fenarimol in Grapes, Grape Must and Wine following Application of Rubigan 12 SC (EAF 383) to Grape Vines Germany 1992/93. GHE-P-3655 Aug 1994.

NH 12. Dow Elanco Ltd. Residues Studies - Grapes - Germany and France 1981/2 Apr 1983.

NH 17. Day, E.W. Fenarimol Residue Data on Grapes and Grape Products from Experiment conducted in the United States in 1983 March 1984 I-EWD-84-03.

NH 20. Day, E.W. and West, S.D. 1988 Fenarimol Residue Trials in Grapes AAC8818 Dec 1988.

NH 22. Trevallyn-Jones, J. Further Submission to T.C.A.C - Withholding Period in Grapes treated with RUBIGAN (contains Australian Dow Elanco Ltd. Residue data) July 1984.

NH 23. Dow Elanco Ltd. Submission to T.C.A.C - Rubigan Data Supporting Reduction in Withholding Period in Grapes (contains Australian Residue data) July 1987.

NH 24. Dow Elanco Ltd. 1995. Residues of fenarimol in fresh and processed grapes after treating Cabernet Sauvignon and Sultana grapevines with Rubigan 120 EC®. March. Ref.

NI 01. Dow Elanco Ltd. Residue Study - Artichoke - Italy 1979 179-250.

NI 05. Butcher, S. Residues of Fenarimol in Globe Artichokes at Intervals following Multiple Applications of RUBIGAN 12 SC (EAF383), Italy 1995 GHE-P4010 Jan 1995.

NJ 01. Butcher, S. and Perkins, J. Residues of fenarimol in Hops and related fractions from the brewing process following application of Drawisan 6WP (EAF 219) - Germany 1990. GHE-P-2517 Oct 1991.

NL 02. Catta-Preta, R.F. and Matos, J.C. Residues of Fenarimol and its Major Metabolites in Bananas following Multiple treatments with Rubigan Ec Fungicide - Costa Rica, Honduras and Ecuador, 1992 April 1993 GHB-P 151.

NL 03. Ishikura, H. Residues of Fenarimol in Pulp, Peel and Whole Bananas Following application of Rubigan 12EC Fungicide in the Philippines - 1991 July 1991. GHF-P -1126.

NL 04. Day, E.W. Reasonable Grounds in Support of the

Petition for the Establishment of A Tolerance for Fenarimol and its Metabolites in or on Bananas. Aug 1993. ECL93073.

NM 01. Decker, O.D. Fenarimol Residues on Pecans when Rubigan 1EC or Rubigan 1AS is Foliar applied to Pecan Trees on Disease Control March 1983 I-ODD-82-02.

NM 02. Decker, O.D. Fenarimol Residues on Pecans when Rubigan is Foliar applied to Pecan Trees for Disease Control Feb 1984 I-ODD-84-01.

OR 01A. Griggs, R.D and Decker, O.D. Determination of Fenarimol in Agricultural Crops and Soil Jan 1981 AM-AACA-R039-AA-755.

OR 01B. Griggs, R.D. and Decker, O.D. Determination of Fenarimol in Agricultural Crops and Soil Jan 1985 AM-AA-CA-RO39-AB-755.

OR 10. Dow Elanco Ltd. Determination of EL-222 in Agricultural Crops and Soils by Gas-Liquid Chromatography Std An.Method No.86 Sep 1976.

OR 11. Dow Elanco Ltd. Determination of Fenarimol In Agricultural Crops (Other than Cereals) by Gas-Liquid Chromatography Nov 1977 Std.An.Method No.97.

OR 19. Yordy, D.W. and Turner, L.G Determination of Fenarimol In Meat, Milk and Eggs. AM-AA-CA-RO72-AA-755 Sep 1982.

OR 20. Butcher, S.M. and Perkins, J.M. Determination of Fenarimol Residues in Fresh, Dried and Spent Hops. ERC91-8 Jan 1992.

OR 21. Butcher, S.M. Determination of Fenarimol Residues in Beer and Spent Yeast. Jan 1992 ERC91-10.

OR 22. Butcher, S.M. and Long, T.J. Determination of Residues of Fenarimol in Grape Must, Wine and Grapes. ERC93-6 Jul 1993.

OR 24. Butcher, S.M. Determination of Residues of Fenarimol in Tomatoes, Peaches and Melons ERC 94.3 Aug 1994.

OR 27. Turner, L.G. Dow Elanco Ltd. Residue Method Development Report for Fenarimol and its Metabolites in Whole Bananas and Banana Pulp. GH-C-2840 Aug 1992.

R 28. Catta-Preta, R.F. and Matos, J.C Determination of Residues of Fenarimol, Compound 212746 and 210302 in Banana Whole Fruit and Pulp BRC 92.2 March 1993.

FENPROPIMORPH (188)

EXPLANATION

Fenpropimorph is a fungicide whose major use is to control diseases in cereals. It was reviewed for the first time at the 1994 JMPR which considered toxicological aspects. An ADI of 0-0.003 mg/kg bw was allocated. Owing to the late receipt of data, the review of residue and analytical aspects was postponed until 1995.

IDENTITY

ISO common name: fenpropimorph

Chemical name

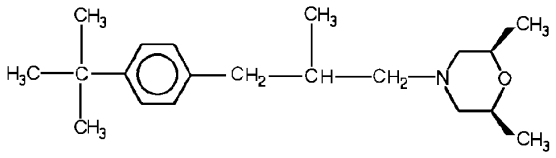
IUPAC:(±)-*cis*-4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-2,6-dimethylmorpholine

CA: *cis*-4-[3-[4-(1,1-dimethylethyl)phenyl]-2-methylpropyl]-2,6-dimethylmorpholine

CAS No.: 67564-91-4

Synonyms: 108406; BAS 421 F (BASF); Ro 14-3169 (Maag); CA 101031 (Ciba)

Structural formula:



Molecular formula: $C_{20}H_{33}NO$
Molecular weight: 303.5

Physical and chemical properties

Pure active ingredient

Vapour pressure:	3.5×10^{-3} Pa at 20°C (BASF, 1988a)		
Melting point:	colourless liquid		
Boiling point:	120°C (at 0.067 mbar)		
Octanol/water partition coefficient:	log P_{OW} =	4.1 (22°C, pH 7) 2.6 (22°C, pH 5) (Keller, 1986)	
Solubility:	Water	7.3 mg/l (20°C, pH 4.4) (BASF 1988b) 5.1 mg/l (unbuffered)	(Rüdel 1988)
		4.3 mg/l (20°C, pH 7)	(BASF 1988c)
		3.5 mg/l (20°C, pH 9-11)	(BASF 1988c)

Toluene>1 kg/kg at 20°C
Ethanol >1 kg/kg at 20°C
Acetone>1 kg/kg at 20°C

Specific gravity: not stated (see density of technical material below)

Hydrolysis (half-life): >64 days 50°C (pH 5, 7, 9) (BASF 1983)
>64 days 70°C (pH 5)
15 days 70°C (pH 7, 9)

No hydrolysis half-life could be determined when fenpropimorph was incubated at pH 3, 5, 7 and 9 in the dark at 25°C for 32 days (Rüdel, 1988). Although it was concluded that fenpropimorph is hydrolytically stable, losses of 20-35% of radioactive material were observed, especially at pH 9 after 20 days incubation. The loss was attributed largely to either increased volatility or adsorption to the glass walls of the container or stopper owing to reduced solubility at higher pH.

Although no hydrolysis products were detected by TLC, fenpropimorph hydrochloride was detected at pH 3 and a compound with similar TLC characteristics to 4-[3-(4-*tert*-butylphenyl)-2-methyl-1-oxopropyl]-*cis*-2,6-dimethylmorpholine (BF 421-13: see Table 1) was found at pH 9.

Photolysis: Stable in artificial sunlight (≥290 nm) up to 30 days at pH 5 and 25°C (Herrchen, 1988a)

Technical material

Purity	Minimum 93% fenpropimorph (reported to JMPR, undocumented).
Melting range:	Liquid
Boiling point:	>250°C at 1 atm (discoloration at 190-210°C) (Ciba, 1992)
Stability:	No information provided.
Density:	0.933 g/cm^3 (Ciba, 1992)

Formulations

Fenpropimorph is a fungicide which has found its most important use for the control of powdery mildew and rust in cereals, and of barley leaf blotch. It is also reported to be active as a post-harvest dip against *Penicillium* fungi, *Alternaria citri*, *Diplodia spp*., and *Phomopsis citri* in citrus, although it is not recommended for this use (Lafuente *et al*., 1986). It is formulated into 49 fungicidal products, alone as an emulsifiable concentrate (750 g ai/l) or with one or two additional active ingredients as an EC, soluble concentrate (SC) or wettable powder (WP). Other fungicides in mixed formulations include propiconazole, fenpropidin, fenbuconazole, chlorothalonil, carbendazim, mancozeb, tridemorph, prochloraz, epoxiconazole and flusilazole. The concentrations of the active ingredients included in all 49 products were provided to the Meeting. The fenpropimorph concentration in mixed formulations is less than when fenpropimorph is formulated alone (118-563 g/l instead of 750 g/l). The total active ingredients in formulations never exceed 750 g/l. Registered uses are listed in Table 17.

METABOLISM AND ENVIRONMENTAL FATE

Table	SUBJECT
1.	Names and structures of fenpropimorph and related compounds
2.	Goats - material balance

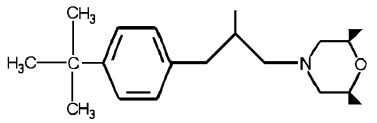
3. Goats - residue distribution
4. Poultry - material balance
5. Poultry - residue distribution (total residue)
6. Poultry - residue distribution (metabolites)
7. Plant and animal metabolites (summary)
8. Barley metabolism
9. Rotational crops - distribution of ^{14}C
10. Spring wheat metabolism (morpholine label)
11. Spring wheat metabolism (morpholine and phenyl labels)
12. Soil - half-lives
13. Degradation in water-sediment systems (laboratory)
14. Degradation in water-sediment systems (field)

Information was provided on the fate of residues in animals, plants, soil, water, and water-sediment systems. Structures, codes and chemical names of fenpropimorph and its degradation products are shown in Table 1. Oxidation is common to all the degradation routes. The metabolism of fenpropimorph in plants is similar to that in animals to the extent that oxidation is the first step and is followed by degradation of the morpholine ring. There are differences (see especially Table 11) in that fenpropimorph is generally the main residue in plants but is not found in animals except in hen kidneys, whereas BF 421-3, BF 421-4, BF 421-16 and BF 421-17 (and/or their conjugates) are metabolites in animals but have not been reported in plants. The plant metabolites BF 421-2-Me, BF 421-7, BF 421-10, BF 421-13 and BF 421-15 have not been reported in animals, although in plants most of these would be at levels below one quarter of the level of the parent compound. An exception may be BF 421-7 (the hydroxypropylamine) which has been reported at a similar level to the parent compound in wheat straw under some conditions.

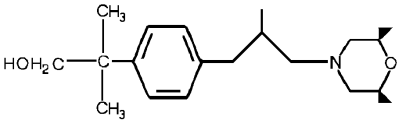
Under neutral conditions fenpropimorph is largely stable in water. Under field conditions degradation in soil proceeds by oxidation and opening of the morpholine ring to give BF 421-2 (the acid), BF 421-7, BF 421-8 (the hydroxyethylamine) and BF 421-10 (dimethylmorpholine). In aerobic water/soil systems the degradation is similar except that the morpholine ring is not opened. In addition to these compounds, BF 421-13 (the alkyl ketone) and BF 421-15 (the morpholine-3-one derivative) can be formed by photolysis of fenpropimorph in soil.

The metabolites referred to by codes are identified below (Table 1).

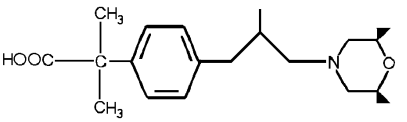
Table 1. Fenpropimorph metabolites, degradation products and related compounds - structures, chemical names and codes.



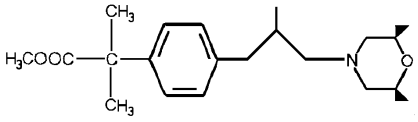
fenpropimorph



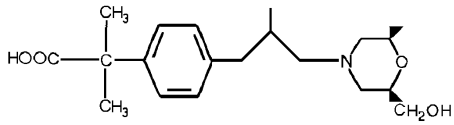
BF 421-1 4-{3-[4-(2-hydroxy-1,1-dimethyl)ethylphenyl]-2-methylpropyl}-*cis*-2,6-dimethylmorpholine



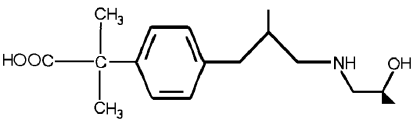
BF 421-2 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid



BF 421-2-Me methyl 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionate

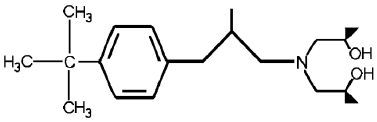


BF 421-3 2-methyl-2-{4-[2-methyl-3-(*cis*-2-hydroxymethyl-6-methylmorpholin-4-yl]propyl)phenyl}propionic acid

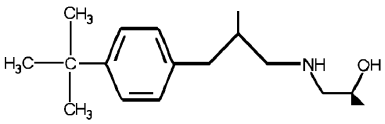


BF 421-4 2-methyl-2-{4-[2-methyl-3-(2-hydroxypropyl)aminopropyl]-phenyl}propionic acid

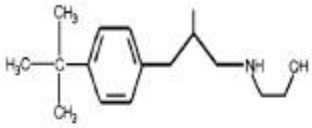
BF 421-6 [3-(4-*tert*-butylphenyl)-2-methylpropyl]bis(2-hydroxypropyl)amine



BF 421-7 [3-(4-*tert*-butylphenyl)-2-methylpropyl](2-hydroxypropyl)amine

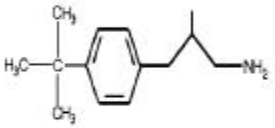


orph



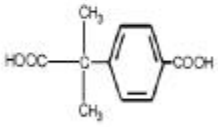
BF 421-8 [3-(4-*tert*-butylphenyl)-2-methylpropyl](2-hydroxyethyl)amine

BF 421-9 2-methyl-3-(4-*tert*-butylphenyl)propylamine

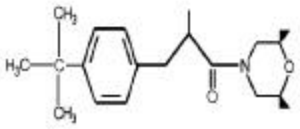


BF 421-10 *cis*-2,6-dimethylmorpholine

BF 421-12 2-methyl-2-(4-carboxyphenyl)propionic acid

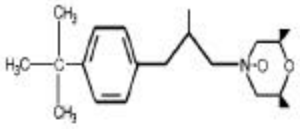


BF 421-13 4-[3-(4-*tert*-butylphenyl)-2-methyl-1-oxopropyl]-*cis*-2,6-dimethylmorpholine



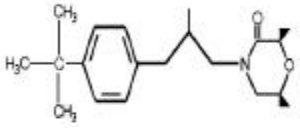
BF 421-14 4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-*cis*-2,6-dimethylmorpholine *N*-oxide

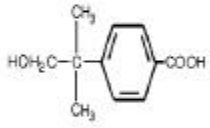
BF 421-15 4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-*cis*-2,6-dimethylmorpholine-3-one

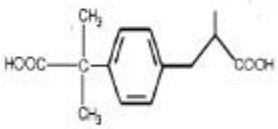


BF 421-16 2-methyl-2-[4-(carboxyphenyl)]propan-1-ol

BF 421-17 2-methyl-2-[4-(2-carboxypropyl)phenyl)]propionic acid







Animal metabolism

The fate of residues was studied in rats, goats and poultry. Metabolism is similar but not identical, consisting mainly in progressive oxidation of *tert*-butyl, methylpropyl and morpholine-methyl groups. Further metabolism of the morpholine ring is demonstrated by the expiration of significant amounts of $^{14}CO_2$ by rats. The expiration of $^{14}CO_2$ was not measured in goats or hens.

Rats. Because material balance and metabolism studies in rats (von der Mühll and Gätzi, 1979; van Dijk and Vogel, 1989; Pryde *et al.*, 1979, 1980) with both morpholine- and phenyl-labelled fenpropimorph were described in the 1994 toxicological evaluation they are not considered in detail here. In summary, 64-72% of the ^{14}C from the morpholine label was excreted within 96 hours after its administration (mostly in faeces and urine) and as much as 12% in expired air (showing breakdown of the morpholine ring). Tissue residues were highest in the liver and somewhat lower in fat. Elimination in the faeces and urine was even higher from the phenyl-labelled compound. No residues of fenpropimorph were reported. Qualitatively the following metabolites were reported (see especially van Dijk and Vogel, 1989).

Metabolite*		Urine	Faeces	Bile	Liver	kidney	Plasma
BF 421-2	+	+	+	+	+	+	
BF 421-3	+	+	-	+	+	+	
BF 421-3 conj.	+	+	+	-	-	-	
BF 421-4**		+	-	-	-	-	-
BF 421-16		+	+	-	-	+	-
BF 421-17		+	-	-	-	+	-

* See Table 1

** Described as "U3-1, probably identical to ... BF 421-4". Tentatively confirmed by TLC

Goats. Three studies were available, the first on the distribution of radioactive residues in milk (and other fluids) and tissues (Hawkins *et al.*, 1980a), the second a supplementary study (on the same animals) of the excretion in faeces and urine (Hawkins *et al.*, 1980b) and the third on the distribution, degradation and excretion of radioactive residues (Ritter, 1989a).

In the first study (Hawkins *et al.*, 1980a) two lactating goats of approximately 56 kg were administered daily by gelatin capsule for ten consecutive days 1.6 mg of [^{14}C]fenpropimorph hydrochloride labelled in the morpholine ring (1.5 mg free base = 0.03 mg/kg bw). Although the feed consumption was not recorded, the dosage would approximate 0.6 ppm in the feed if all of the daily offering of 1.5 kg hay and 1 kg concentrate was consumed. Treated goats and an untreated control were milked twice daily, immediately before dosing and 6 hours after dosing, then 24 hours after the last dose and just before slaughter. Blood samples were taken at several hourly intervals and 24 hours after the last dose, and samples of bile were retained. Twenty four hours after the last dose samples of liver, kidneys, heart, brain, muscle and fat were also taken. Analyses were by liquid scintillation counting. Approximately 1.5 to 2% of the daily dose was eliminated in the milk with mean residues (combined milk samples before dosing and 6 hours after dosing) reaching a plateau at approximately 7 to 8 ng/ml (ppb) (9 ng/ml maximum) after 4 to 6 days. A similar profile and concentration were observed in plasma and a similar profile but lower levels in whole blood. Maximum and average residues (fenpropimorph equivalents) in the fluids and tissues from the two goats 24 hours after the last dose were as shown below

Tissue	ng/g or ng/ml	
	Max.	Mean
Liver	103	96
Kidneys	29.4	28.5
Brain	12.4	12
Heart	8.3	8.2
Fat (back)	7.6	7
Fat (omental)	12	9.6
Muscle (leg)	3.4	3.1
Muscle (loin)	4	3.9
Bile	1618	1264
Plasma	7	6.9
Milk	8.4	8.4
Blood	5.4	5.3

In the supplementary study with the same goats (Hawkins *et al.*, 1980b) the authors reported daily urinary excretion of radioactivity increasing from about 13% of the administered dose after 24

hours to 32 and 39% after 6 or 7 days. Elimination in the faeces increased from 16 to 24% of the daily dose during the first 24 hours to 70-73% after 7 days. Over the 10-day dosing period the average cumulative elimination of administered radioactivity for the two goats was 26.7% in the urine and 57.5% in the faeces, giving a total of 84.2%. Residues in the urine remained constant after about 7 days, but continued to increase in the faeces through the tenth day.

In the third and most comprehensive study (Ritter, 1989a) performed according to GLP guidelines, two goats were dosed orally by stomach tube for 5 consecutive days with either [^{14}C]phenyl-labelled fenpropimorph (2335 ppm daily in the feed = 55.5 mg/kg bw/day) or with [^{14}C]morpholine-labelled fenpropimorph (labelled adjacent to the ring oxygen) (1421 ppm daily in feed = 54.6 mg/kg bw/day). The test material was stable over the period of the study.

Blood samples were taken daily one hour after dosing and after the last dose. The goats were milked twice daily, 1 and 8 hours after dosing (1 and 4 hours after the last dose) and urine and faeces samples were taken at regular intervals. The animals were slaughtered 5 hours after the last treatment and samples of heart, liver, kidneys, spleen, teat, brain, muscle, fat and bile were taken for analysis, mainly by scintillation counting and silica gel TLC (8 different solvent systems with 15 reference compounds). TLC of methylated metabolites and hydrolysed conjugates was also used in comparing metabolites and standards. The material balance of the radioactivity is shown in Table 2.

Table 2. Material balance of radioactivity from lactating goats administered [^{14}C]phenyl- or [^{14}C]morpholine-labelled fenpropimorph daily for 5 days (Ritter, 1989a).

Sample	% of administered radioactivity	
	Goat 1, phenyl label	Goat 2, morpholine label
Urine	14.49	21.34
Faeces	20.43	28.95
Cage wash	1.02	0.44
Milk	0.06	0.32
Tissues and organs[1]	2.65	3.13
Bile	1.80	1.08
Total[2]	40.45	55.26

[1] Assumes fat and muscle are 12 and 40% respectively of body weight
[2] The author assumed that most of the remaining radioactivity was in the gastrointestinal tract.

The radioactivity in the whole blood and plasma increased steadily from 6.8 and 9.2 mg/kg fenpropimorph equivalents for the phenyl label and 2.5 and 3.1 mg/kg for the morpholine label 1 hour after the first dose to 54 and 93 and 29 and 40 mg/kg respectively 5 hours after the last dose. BF 421-2 was the most prominent metabolite in protein-free plasma with both labels (52-58% of the recovered radioactivity) followed by BF 421-3 (0.6-3%) with other unidentified metabolites ≤7%.

A significant level of radioactivity in the bile indicated biliary excretion. This was confirmed in a 5-day feeding study with the highest residues found in the faeces (20-29% of the total administered radioactivity) with slightly less in the urine (15-21%). The elimination of radioactivity in the faeces or urine was highest from the phenyl label 48 hours after the first administration (after the 2nd treatment), whereas it was at its highest from the morpholine label 96 hours after the first administration (after the 4th treatment).

A relatively low level of radioactivity was found in the milk (0.06% from the phenyl label, 0.3% from the morpholine label) and organs and tissues (about 3% from both labels), although only 40 to 55% of the administered radioactivity was accounted for in the urine, faeces, cage wash, milk, organs, tissues and bile. The rest was assumed to be in the gastrointestinal tract.

Residues in milk (ì g parent equivalents/ml) from the phenyl label increased from 0.7 and 2.9 ì g/ml 1 and 8 hours after the first administration to 6.9 and 9.7 ì g/ml and 1 and 8 h after the fourth, decreasing to 1.9 and 0.9 ì g/ml 1 and 4 hours after the fifth. For the morpholine label residues were similar at 0.7 and 3.9 ì g/ml 1 and 8 hours after the first dose and 11 and 19 ì g/ml after the fourth but continued to increase to 16 and 23 ì g/ml 1 and 4 hours after the fifth. From the phenyl label 76.2 and 23.8% of the radioactivity was in the whey and protein fractions of the milk respectively and from the morpholine label 60 and 4.7%. A further 6.6% of the radioactivity from the morpholine label was in a hexane fraction and 28.7% was unextracted.

The distribution of identified and unidentified metabolites in the urine, faeces, milk and tissues is shown in Table 3.

Table 3. Distribution of identified and unidentified metabolites in excreta, milk and tissues of lactating goats dosed daily for 5 days with phenyl- or morpholine-labelled [^{14}C]fenpropimorph[1] (Ritter, 1989a).

Sample	% Extract-able ^{14}C	BF 421-1[1]		BF 421-2[1]		BF 421-3[1]		Unidentified metabolites		
		% of recov'd ^{14}C	ì g/g[2]	% of recov'd ^{14}C	ì g/g[2]	% of recov'd ^{14}C	ì g/g[2]	No.	% of recov'd ^{14}C	ì g/g[2]
Phenyl label										
Urine	-	-	-	-	-	20.1	193	9	2.1-17	20-160
Faeces[3]	83-86	38	924	-	-	9.4	229	5	2.1-13	51-310
Faeces[4]	83-86	12	1.4	12	1.4	-	-	6	3.8-18	0.5-2.2
Muscle[5]	96	-	-	68	6	-	-	5	3.4-6.5	0.3-0.6
Liver	92	-	-	33 6.7[6] 31[6]	47 9.4[6] 43[6]	-	-	2	9-12	13-17
Kidneys	99	-	-	11	25	6.3	15	4	11-34	25-78
Fat[5]	96	25	1.1	38	1.6	-	-	5	1.9-17	0.1-0.8

Sample	% Extract-able ^{14}C	BF 421-1[1]		BF 421-2[1]		BF 421-3[1]		Unidentified metabolites		
		% of recov'd ^{14}C	ì g/g[2]	% of recov'd ^{14}C	ì g/g[2]	% of recov'd ^{14}C	ì g/g[2]	No.	% of recov'd ^{14}C	ì g/g[2]
Milk whey[7]	-	-	-	-	-	-	-	6	5-22	0.2-0.6
Morpholine label										
Urine	-	-	-	-	-	43	136	7	1.7-20	5.4-61
Faeces [3]	86-88	7.6	139	53	973	12	214	3	3.4-5.8	63-107
Faeces[4]	86-88	4.7	153	60	1949	9.7	314	2	4.6-8.4	147-273
Muscle[5]	86	-	-	64	4	-	-	3	4.2-12	0.3-0.8
Liver	84	-	-	40 32[6]	50 40[6]	-	-	2	4.2-7.6	5.2-9.5
Kidneys	90	-	-	27	14	11	5.8	5	2.2-28	1.2-15
Fat[5]	64	27	5	3	0.6	0.9	0.2	6	0.9-22	0.2-4
Milk whey[7]	-	-	-	17	6.5	7.2	2.8	3	6-24	2.3-9.2

[1] See Table 1
[2] Fenpropimorph equivalents; faeces fresh weight
[3] Sampled from 1st to 4th dose
[4] Sampled 5 hours after 5th dose
[5] Assumes fat and muscle are 12% and 40% respectively of body weight.
[6] Conjugated. Confirmed by hydrolysis, methylation, and TLC co-chromatography.
[7] Sampled 1 and 4 hours after last dose

A high percentage of the radioactivity (≥83%) was extractable from most substrates. No parent compound was identified in any sample with either label and all samples contained from 2-9 unidentified metabolites. BF 421-3 was the only identified metabolite in urine from either label. BF 421-1, BF 421-2 and BF 421-3 were identified in the faeces from both labels. BF 421-2 was the only identified metabolite in the muscle and liver. In the liver two conjugated metabolites of BF 421-2 were also observed. The identified metabolites (predominant compound underlined) were BF 421-2 and BF 421-3 in the kidneys; BF 421-1, BF 421-2 and BF 421-3 in the fat from the morpholine label, but only BF 421-1 and BF 421-2 from the phenyl label; BF 421-2 and BF 421-3 in milk whey from the morpholine label with none from the phenyl label, although 6 unidentified metabolites were observed.

Poultry. In a study in accordance with GLP, two groups of ten white leghorn hybrid laying hens were dosed once daily for five days by syringe intubation with about 6.8 mg/hen (3.9 mg/kg bw) of [^{14}C]fenpropimorph labelled in the phenyl or morpholine ring. Based on average feed consumption the doses were equivalent to 51.5 ppm in the diet for phenyl label and 39.3 ppm for the morpholine label. These levels are respectively 206 and 157 times the dietary intake calculated to result from maximum residues of 0.5 mg/kg in grain consumed as 50% of the diet (Ritter, 1989b).

Eggs were collected twice daily (before and 8 hours after dosing) and before slaughter, and separated into yolks and whites which were pooled by group and sampling interval. The faeces were collected and pooled in a similar manner, although sampled only once daily. At slaughter (5 hours after the last dose for treated hens) blood samples were taken and analysed within 24 hours, and samples of kidneys, liver, muscle, gizzard, heart, brain, fat, skin (+ subcutaneous fat), ovaries and spleen were taken for analysis. Samples were analysed by scintillation counting for material balance and distribution, and characterized by TLC against reference standards before and after acidic hydrolysis. The material balance of administered radioactivity is shown in Table 4 and its distribution among tissues in Table 5.

Table 4. Material balance of radioactivity from laying hens administered [^{14}C]phenyl- or [^{14}C]morpholine-labelled fenpropimorph daily for 5 days (Ritter, 1989b).

Sample	% of administered radioactivity	
	Group 1, phenyl label	Group 2, morpholine label
Excreta	83.1[1]	79.1[2]
Cage wash	3.6	2.7
Eggs	0.2	0.4
Tissues, organs, blood[3]	3.1	3.6
Total	90	85.8

[1] 93% of recovered radioactivity extracted
[2] 88.1% of recovered radioactivity extracted
[3] Assumes muscle, fat and blood are 40, 12 and 8% of body weight respectively.

Table 4 illustrates the predominant and rapid elimination in the excreta, as in goats and rats, and the low proportion of the administered dose retained in the tissues.

Table 5. Distribution of residual radioactivity in tissues, eggs and blood of laying hens dosed daily for 5 days with phenyl- or morpholine-labelled [^{14}C]fenpropimorph (Ritter, 1989b).

Sample	Phenyl label			Morpholine Label		
	% extractable[1]	% of total dose	mg/kg[2]	% extractable[1]	% of total dose	mg/kg[2]
Egg white[3]	--	0.008	0.17[4]	--	0.02	0.42[5]
Egg yolk[3]	--	0.02	0.83[6]	--	0.09	3[4]
Liver	87	0.38	2.8	76	0.55	3.9
Kidneys	87	0.11	2.8	70	0.10	2.4
Muscle (chest)	--	0.58	0.28	--	0.52	0.24
Muscle (Leg)	97	0.91	0.42	67	0.73	0.34
Gizzard	88	0.05	0.40	69	0.12	1.1
Heart	--	0.02	0.93	--	0.01	0.71
Brain	--	<0.01	0.16	--	<0.01	0.31
Fat (stomach)	99	0.95	1.4	97	0.70	1.1
Skin (+ subcut. fat)	96	0.01	0.97	92	0.01	0.68
Ovaries	--	0.29	1.3	--	0.94	4.2
Spleen	--	0.01	0.82	--	0.01	1.5
Blood	--	0.6	1.4	--	0.47	1.1
Plasma	--	--	1.9	--	--	1.3

[1] Extractable ^{14}C as % of ^{14}C in sample
[2] As fenpropimorph equivalents
[3] 5 hours after last dose
[4] 79.7% of radioactivity in protein-free fraction and 20.3% in protein
[5] 21.6% of radioactivity in protein-free fraction and 78.45 in protein
[6] 62% of radioactivity in protein-free fraction and 37.2% in protein

Table 5 shows the high percentage of the radioactivity extractable from the tissues and blood. The highest residues from the phenyl label (about 3 mg/kg) were found in the liver and kidneys, with about 1-1.5 mg/kg in the fat, ovaries, skin, heart and blood and lower levels in muscle and other tissues. The highest residues from the morpholine label were found in the ovaries, liver, egg yolk and kidneys in that order with lower levels in the fat, gizzard, spleen, blood and heart and little in muscle. Residues in the whites of eggs from both labels reached a plateau approximately 48 hours after the first dose, whereas in the yolks they continued to increase throughout the collection period.

Although 3-10 unidentified metabolites were detected and measured as fenpropimorph equivalents in the organosoluble or water-soluble fractions of the excreta, eggs, muscle, fat, skin and gizzard, compounds were identified and determined only in the plasma, liver and kidneys, with the results shown in Table 6.

Table 6. Distribution of identified and unidentified compounds in plasma, liver and kidneys of laying hens dosed daily for 5 days with phenyl- or morpholine-labelled [^{14}C]fenpropimorph (Ritter, 1989b).

Sample	fenpropimorph		BF 421-1[1]		BF 421-2[1]		BF 421-3[1]		Unidentified metabolites		
	% of recov'd ^{14}C	mg/kg	% of recov'd ^{14}C	mg/kg[2]	% of recov'd ^{14}C	mg/kg[2]	% of recov'd ^{14}C	mg/kg[2]	No.	% of recov'd ^{14}C	mg/kg[2]
Phenyl label											
Liver (org. sol.)			--	--	--	--	--	--	10	2.2-13	0.06-0.36
Liver (H_2O sol.)			--	--	--	--	--	--	8	0.8-6.3	0.02-0.17
Plasma			--	--	13	0.24	--	--	5	5.5-30	0.1-0.56
Kidneys (org. sol)	11	0.31			3.5	0.1	1.9	0.05	6	1.5-4.7	0.05-0.13
Kidneys (H_2O sol)			--	--	--	--	--	--	5	1.2-21	0.03-0.6
Morpholine label											
Liver (org. sol.)			--	--	3.9	0.15	--	--	5	3.8-21	0.15-0.83
Liver (H_2O sol.)			--	--	--	--	--	--	8	1.1-5.9	0.04-0.2
Plasma			2.3	0.03	12	0.16	--	--	5	3.2-25	0.04-0.33
Kidneys (H_2O sol)			--	--	--	--	--	--	3	9.9-15	0.23-0.36

[1] See Table 1
[2] fenpropimorph equivalents

Table 6 shows the (phenyl-labelled) parent compound to be found only in the kidneys (analyses of the organosoluble fraction were not provided for the morphine label). BF 421-1 was found in the plasma (morpholine label) but not in the liver or kidneys. Metabolite BF 421-2 was found in the kidneys and liver (morpholine label) and BF 421-3 only in the kidneys.

The metabolites found in rats, goats, hens and wheat plants are listed in Table 11 at the end of the section describing metabolism in plants.

The studies show a similar metabolic fate in rats, goats and hens. Residues of the parent compound were detected only in hen kidneys. BF 421-1 was detected in goats and hens, but not in rats. No conjugates were detected in hens, but conjugates of BF 421-2 were found in goats and of BF 421-3 in rats. Metabolites BF 421-16 and -17 were detected only in rats. On the basis of reported studies the proposed metabolic fate of fenpropimorph in animals is as shown in Figure 1.

Plant metabolism

The metabolism of fenpropimorph in plants is similar to that in animals to the extent that oxidation is followed by degradation of the morpholine ring, but certain metabolites are found in animals and not in plants and vice versa.

The fate of fenpropimorph in plants was investigated in four studies: one on barley (Pryde and Etterli, 1979), one crop rotation study with spinach, sugar beet and wheat (Pryde and Etterli, 1980) and two metabolism studies on wheat (Huber, 1979a; Rüdel, 1990).

In the first study Pryde and Etterli (1979) grew summer barley under greenhouse conditions and treated leaves by syringe at the five-leaf tillering stage with [^{14}C]fenpropimorph (free base) labelled at the benzylic carbon between the rings. The specific activity was 152 ì Ci/mg and application was at a rate equivalent to 0.9 kg free amine/ha (5000 l/ha). The goal was to determine the dissipation and translocation of total radioactivity and of fenpropimorph from topical applications. Treated and untreated leaves from the same plant as well as untreated leaves from controls were sampled at intervals. Surface residues were removed for analysis by stirring the leaves with a mixture of HC1 and methanol and the washed leaves were then macerated with the same mixture and filtered.

Radioactivity was measured and characterized by combustion, scintillation counting, TLC on alumina and silica, with radio scanning, and HPLC. Whole plants were examined by autoradiography. Results are shown in Table 7.

Table 7. Distribution of total radioactivity and fenpropimorph in or on barley leaves from plants treated with [^{14}C]fenpropimorph (Pryde and Etterli, 1979).

Days after treatment	^{14}C residues				
	Treated leaves				Other green plant parts (untreated)
	Surface wash		Washed leaves		
	Extracted radioactivity, % of applied	fenpropimorph, % of extracted radioactivity[1]	Extracted radioactivity, % of applied	fenpropimorph, % of extracted radioactivity[2]	Extracted radioactivity, % of applied
0	62-65	93	3.1-4.6	87	0.02-0.04

fenpropimorph

Days after treatment	^{14}C residues				
	Treated leaves				Other green plant parts (untreated)
	Surface wash		Washed leaves		
	Extracted radioactivity, % of applied	fenpropimorph, % of extracted radioactivity[1]	Extracted radioactivity, % of applied	fenpropimorph, % of extracted radioactivity[2]	Extracted radioactivity, % of applied
1	45-58	77	5.3-14	69	0.02-0.03
5	49	71	11-12	17	0.06-0.07
8	33-35	70	12	9	0.05-0.12
15	26	57	17-22	6	0.07-0.3
20	9.2-16	63	27-29	7	0.2-1.1

[1] Average of TLC and HPLC results
[2] TLC

fenpropimorph

Figure 1. Metabolic pathways of fenpropimorph in animals.

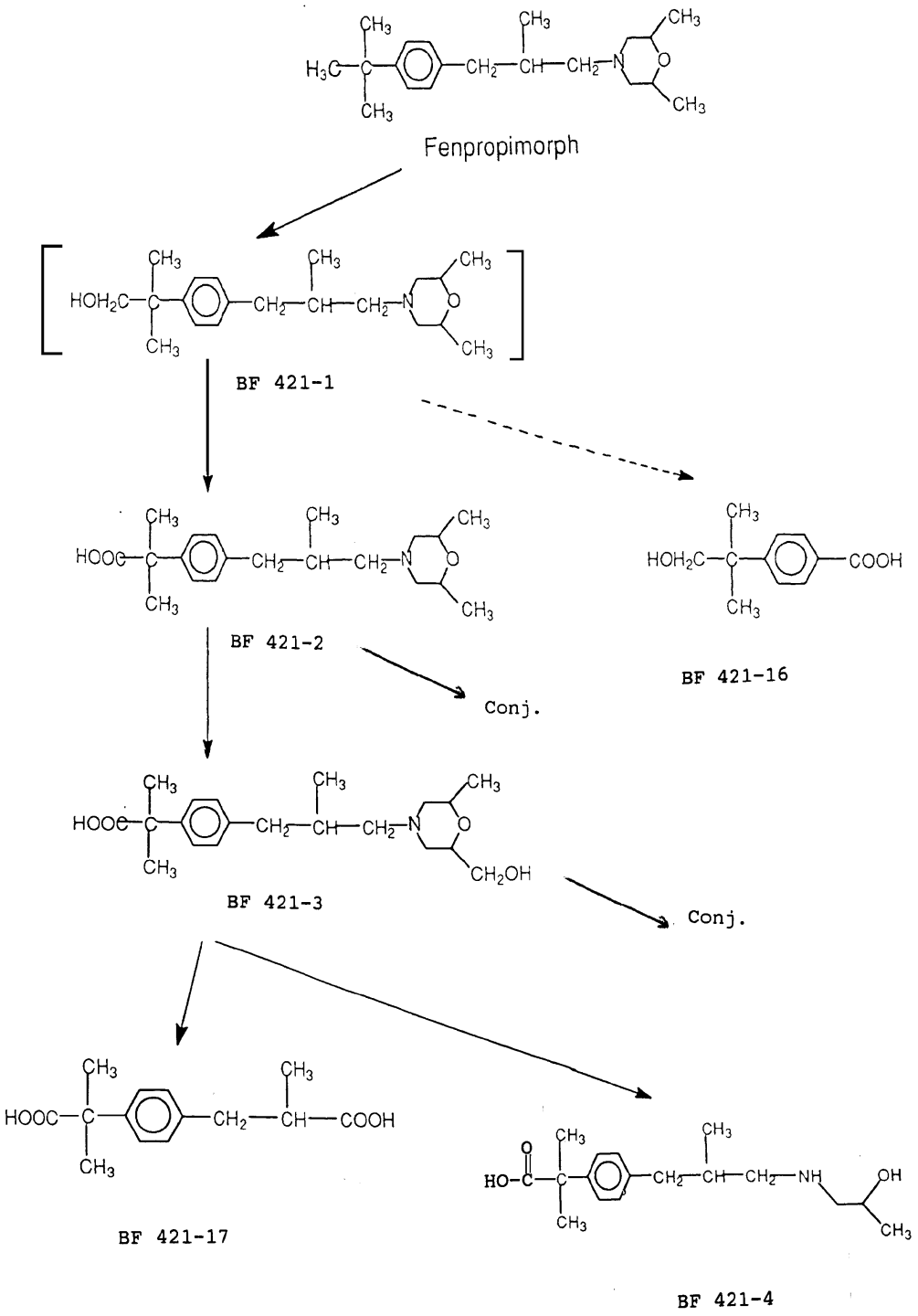


Table 7 shows that up to 65% of the applied radioactivity is on the leaf surface on the day of application and 93% of the surface residue is unchanged fenpropimorph. Even after 20 days up to 16% of the residue is on the surface, of which 63% is fenpropimorph. The proportion of the applied radioactivity remaining in the leaf after washing increased from about 5% on the day of application to almost 30% after 20 days and in the same period the proportion of fenpropimorph decreased from 87% to 7% of the extracted ^{14}C. Although always at low levels, the increase in the radioactivity in untreated plant parts during the test period indicates a limited translocation from the leaves to the roots and uptake into other plant parts. Autoradiography of the plants was reported to confirm that. The decrease in the mean overall recovery of the radioactivity from 67.2% on the day of application to 44.3% on day 20 was attributed to the loss of volatile material.

In the second study (Pryde and Etterli, 1980) spinach, sugar beets and wheat were grown in soil used in a previous wheat metabolism study in which a 1 m^2 plot of sandy loam soil with plants of Probus winter wheat had been spray-treated with [^{14}C]fenpropimorph hydrochloride labelled at the same carbon as before at a rate equivalent to 0.72 kg ai free base/ha (2450 l/ha). The top 5-10 cm depth of soil was used to grow the rotational crops. The plants were grown under greenhouse conditions and both plants and soil were collected at various intervals for measurement of radioactivity by combustion analysis. No grain was produced under the greenhouse conditions, so only the mature wheat plants were analysed. The results are shown in Table 8.

Table 8. Distribution of radioactivity in soil and rotational crops after treatment of soil with [^{14}C]fenpropimorph (Pryde, Etterli, 1980).

Days after treatment of plot	Age of crops (days)	Average total residue, mg/kg fenpropimorph equivalents			
		Soil	Spinach[1]	Sugar beet[2]	Wheat[3]
7	--	0.42	--	--	--
102	10	--	0.010	0.13	0.08
103	11	0.1	--	--	--
105	13	--	0.014	0.15	0.11
109	17	--	0.013	0.11	0.09
112	20	--	0.011	0.11	0.12
116	24	--	--	0.11	0.10
119	27	--	0.010	0.11	0.09
123	31	--	0.011	--	--
126	34	--	0.011	<0.002	0.09
130	38	--	0.009	--	--
144	52	--	0.006	--	--
151	59	--	0.005	--	--
263	171	0.02[4] 0.07[5]		0.01 green plant 0.004 mature beet	<0.02

[1] Fresh wt. basis, 90.6% water
[2] Fresh wt. green plant, 19.1% water, or mature beet (without leaves or roots), 20.6 water
[3] Fresh wt., 19.6% water
[4] Soil from sugar beet pot
[5] Soil from wheat pot

In the third study (Huber, 1979a) Kolibri variety summer wheat was planted (30 seeds/pot) in 36 pots (18 × 18 × 18 cm, 15 cm sandy loam soil) and spray-treated 55 days after seeding with fenpropimorph hydrochloride labelled at the morpholine ring carbons adjacent to the oxygen (specific activity 9.2 mCi/mMol, 60083 dpm/ì g) at a rate equivalent to 1.5 l/ha (1.3 kg ai/ha). Plants were grown in an open greenhouse. Green plants were sampled 21 and 43 days after treatment, and straw and seed at harvest 84 days after treatment. Samples were deep-frozen, then homogenized and stored at -25°C until analysis, for which they were extracted with methanol. Liquid/liquid extraction, liquid chromatography, derivatization, GLC, radio-GLC, radio-HPLC, scintillation counting, and GC-MS were used to characterize and identify the radioactive residues. The results are shown in Table 9.

Table 9. Radioactive residues in spring wheat treated with morpholine-labelled fenpropimorph (Huber, 1979a).

Compound or fraction	Green plant				Straw 84 days		Grain (84 days) "Bound" radioactivity, % of TRR		
	21 days		43 days						
	mg/kg[1]	% of TRR[2]	mg/kg	% of TRR	mg/kg	% of TRR			
Fenpropimorph	3	47	1.7	38	2.6	22			
BF 421-1 (M=319)	0.5	7	0.3	7	0.9	8			
BF 421-7 (M=263)[3]	0.7	12	0.5	10	3.1	26			
BF 421-10 (M=115)	0.2	3	0.1	3	0.3	3			
M=103[3]	0.1	2	0.08	2	0.1	1	Starch	Protein	Polysac-charides
Total of identified compounds	4.5	71	2.7	59	6.9	60	49	16	5
TRR in crop part	6.5	100	4.3	100	11.9	100	0.43 mg/kg[1]		
MeOH-extractable		87		79		62	9%		

[1] As fenpropimorph equivalents
[2] Total radioactive residue
[3] BF 421-10 further degraded

Table 9 shows that both the levels and the extractability of the residues decrease with time. Only about 5-9% of the radioactivity in harvested seeds (0.43 mg/kg fenpropimorph equivalents) was extractable and the very low residues were not identified. Almost half of the unextracted residue was incorporated into the starch, 16% was in a protein precipitate and 5% in the polysaccharide fraction. Of the 40% unextractable radioactivity in wheat straw 21% was found in the lignin fraction.

Fenpropimorph was the predominant residue (38-47% of the TRR) and BF 421-7 the main metabolite (10-12% of the TRR) found in green plants. BF 421-7 was the main residue in straw (26% of the TRR), slightly higher than the parent compound at 22% of the TRR. Lower levels of BF 421-1 and 421-10 were also measured in all plant parts except the grain.

In the fourth study (Rüdel, 1990) spring wheat plants (Ralle variety, 10-12 plants/pot) were treated under field conditions at the tillering stage with both phenyl- and morpholine-labelled fenpropimorph hydrochloride at 0.75 kg ai/ha and harvested according to the following schedule.

	Days	
	Phenyl label	Morpholine label
forage	0	7
	21	28
straw	56	57
grain	56	57
roots	56	57

Samples were extracted with methanol, transferred to water, acidified and extracted successively with hexane, chloroform, acidic ethyl acetate and basic ethyl acetate. The organic extracts were cleaned up by solid-phase extraction or preparative TLC and analysed by 2-dimensional TLC. Major fractions were analysed by GLC with ion-trap detection. The total radioactivity was measured by scintillation counting. Straw samples were also subjected to enzymatic and hydrolytic treatment to release any conjugated compounds. Results are shown in Table 10.

Table 10. Radioactive residues in spring wheat treated with morpholine- and phenyl-labelled [^{14}C]fenpropimorph (Rüdel, 1990).

Compound or fraction	Forage		Straw		Grain		Forage	
	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]	% of TRR	mg/kg[1]
Phenyl label (21 days forage, 56 days straw/grain)							Phenyl label (0 days)	
Fenpropimorph	26.7	2.4	24	2.6				
BF 421-2	0.08	0.01	7	0.8				
BF 421-2-Me &/or BE 421-15	0.3	0.02	0.02	0.00				
BF 421-7 &/or BF 421-1	2.4	0.23	0.4	0.05				
BF 421-13	1.5	0.13	0.2	0.02				
Unidentified metabolites (no.)	0.03-6 (30)	0.00-0.5	0.04-5.6 (37)	0.00-0.6				
Total extractable	61	5.4	61	6.8	12.2	0.01	97	64
TRR	100	8.8	100	10.9	100	0.11	100	66
Morpholine label (28 days forage, 57 days straw/grain)							Morpholine label (7 days)	
Fenpropimorph	16.4	2	20	4.8				
BF 421-1	0.01	0.00						
BF 421-1 &/or BF 421-7			0.3	0.07				
BF 421-2	0.6	0.08	--	--				
BF 421-2-Me &/or BF 421-15	--	--	--	--				
BF 421-7	0.65	0.08						
BF 421-13	0.2	0.03	--	--				
Unidentified metabolites (no.)	0.02-4.4 (33)	0.00-0.6	0.01-12 (43)	0.00-3				
Total extractable	52	6.4	56	14	12.9	0.05	94	38
TRR	100	12.2	100	24	100	0.37	100	40

TRR = total radioactive residue
[1] Fenpropimorph equivalents

At the first sampling (0 or 7 days) almost all of the radioactivity (≥94%) was extractable. As in the Huber greenhouse study, the parent compound was the predominant residue in the forage at harvest. It was also the main residue in the straw, whereas in the Huber study BF 421-7 slightly exceeded fenpropimorph at harvest. Fenpropimorph was confirmed in forage by GC-MS, and metabolites by two-dimensional TLC. BF 421-2, BF 421-7 and/or 421-1, and BF 421-13 were prominent metabolites in the forage. Numerous unidentified metabolites were characterized, no one of which exceeded 0.6 mg/kg fenpropimorph equivalents.

In straw the pattern was generally similar but BF 421-2 was higher than in forage and other metabolites were lower, with fewer identified with the morpholine label. Again numerous unidentified metabolites were found, of which only one (morpholine-labelled) at 3 mg/kg parent equivalents exceeded 0.8 mg/kg. Most of the radioactivity in straw from the phenyl label was associated with the lignin fraction. Hydrolysis of straw before extraction yielded BF 421-1, identified by GC-MS.

Metabolite BF 421-2-Me was reported in forage and straw from the phenyl label, but not from the morpholine label. BF 421-13 was found in the straw from the phenyl but not the morpholine label.

The metabolites found in this study but not reported by Huber were BF 421-2, BF 421-2-Me (phenyl label only), BF 421-13 and BF 421-15 (phenyl label only). There was some difficulty in distinguishing quantitatively between BF 421-1 and BF 421-7 and between BF 421-2-Me and BF 421-15.

Again, only a low level of the radioactivity was found in the grain (≤0.4 mg/kg parent equivalents) and of that less than 13% was extractable. None of the residues in the grain were identified, but little of the radioactivity was found in the protein or polysaccharide fractions (≤8% and ≤1.1% of the TRR respectively). The starch contained about 32% of the TRR, but <3% was found in osazone derivatives.

In combination the cereal plant metabolism studies show oxidation of the *tert*-butyl group to the alcohol and then to the acid, with some methylation of the acid. The morpholine ring is oxidized before its cleavage to form the hydroxypropylamine. A minor route involves oxidation of the *N*-carbon of the methylpropyl group before cleavage of the morpholine ring. The results of these studies are the basis for the proposed metabolic pathway in plants shown in Figure 2.

The components of the residues found in animals and plants are listed in Table 11.

Table 11. Fenpropimorph metabolites found in animals and plants.

Compound (*see* Table 1)	Sites in which compound found (F = forage; S = straw)			
	Rats	Goats	Hens	Wheat plants
Fenpropimorph	--	--	kidneys	F, S
BF 421-1	--	faeces, fat	blood	F, S
BF 421-2	urine, faeces, bile, liver, kidneys, plasma	faeces, muscles, liver, kidneys, fat, milk	blood, kidneys, liver	F, S
BF 421-2 conj.	--	liver	--	--
BF 421-Me	--	--	--	F, S
BF 421-3	urine, faeces, liver, kidneys, plasma	urine, faeces, kidneys, fat	kidneys	--
BF 421-3 conj.	urine, faeces, bile	--	--	--
BF 421-4	urine	--	--	--
BF 421-7	--	--	--	F, S

Compound (*see* Table 1)	Sites in which compound found (F = forage; S = straw)			
	Rats	Goats	Hens	Wheat plants
BF 421-10	--	--	--	F, S
BF 421-13	--	--	--	F, S
BF 421-15	--	--	--	F, S
BF 421-16	urine, faeces, kidneys	--	--	--
BF 421-17	urine, kidneys	--	--	--

Environmental fate in soil

Six studies were provided on the fate of fenpropimorph in soil: photolysis in soil (Herrchen, 1988b), behaviour in soil under field conditions (Hesse and Tilting, 1991, 1992), mineralization (Huber, 1980), aerobic degradation (Huber, 1979b), and dissipation, degradation and leaching under field conditions (von der Mühll *et al*., 1980).

In the photolysis study (Herrchen, 1988b) a loamy sand (pH 5.8, 63 cm^2 surface area, 0.4 cm depth, 40% natural moisture) was treated with 10 mg [^{14}C]phenyl-labelled fenpropimorph/kg soil and irradiated for 30 days with artificial sunlight (xenon lamp filtered to exclude UV below 290 nm) at 1.5 times the intensity of natural sunlight. Residues were determined and characterized by scintillation counting, TLC and HPLC, and the identity of the parent compound was confirmed by MS. After 30 days of irradiation the parent compound had decreased to 50% of the TRR (6.1 mg/kg).

The oxidation products BF 421-13 and BF 421-15 were identified at maximum levels of 9.3% of the TRR (1.1 mg/kg) and 5.3% of the TRR (1.4 mg/kg) respectively after 30 days. Two unidentified compounds were each <6% of the TRR. No volatile products were detected. The half-life of the parent compound was estimated to be about 30 days. The increase in unextractable radioactivity (from 1.6% to 11.9% over 30 days) was taken to be an indication of the sorption of photodegradation products by the soil.

In the field studies (Hesse and Tilting, 1991, 1992; von der Mühll, 1980) several fallow soils at various locations in Germany and one in Switzerland were treated with fenpropimorph at 0.75 or 1.1 kg ai/ha (in *c*. 400 l water/ha), periodically sampled over 14-15 months down to a 1 m depth, and analysed by GLC with a nitrogen FID for fenpropimorph and BF 421-2. Half-lives varied, according to soil type and location, from 10 to 90 days (Table 12).

Figure 2. Metabolic pathways of fenpropimorph in plants.

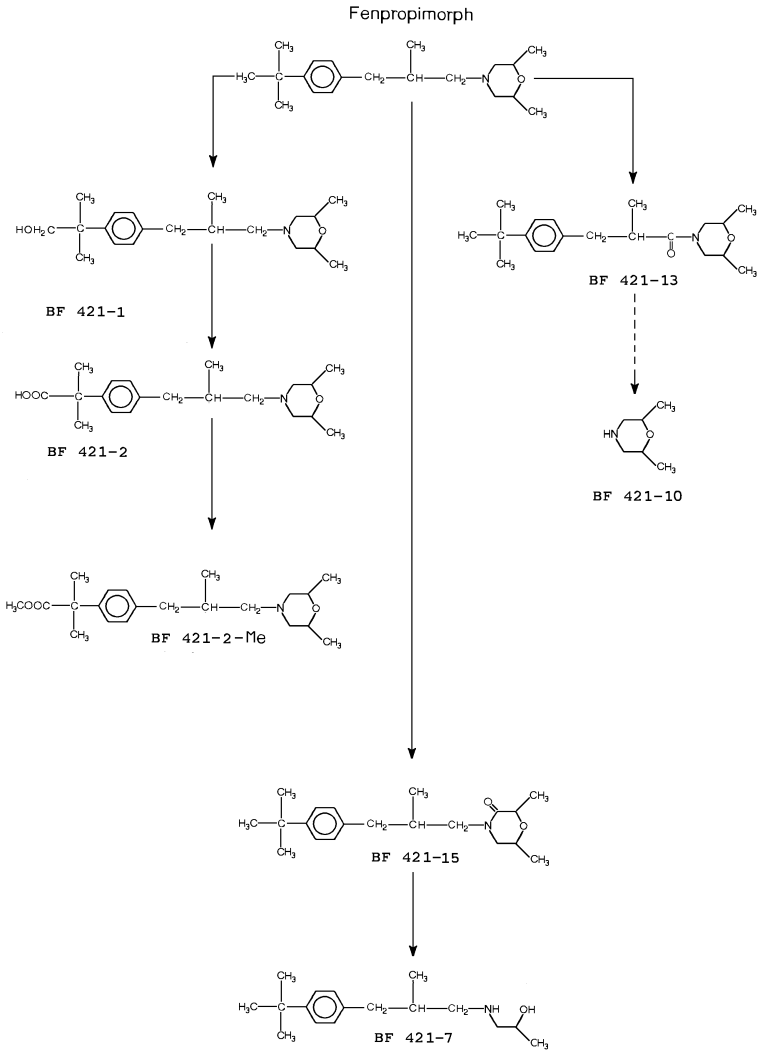


Table 12. Half-lives of fenpropimorph in different soils under field conditions.

Soil type (Location)	Half-life (days)	Application		Reference
		Rate g/ha	Month	
Loam (Niedersachsen, Germany)	40	750	May	Hesse and Tilting, 1991

Soil type (Location)	Half-life (days)	Application		Reference
		Rate g/ha	Month	
Loamy clay (Baden-Württemberg, Germany)	90	750	April	Hesse and Tilting, 1991
Sandy loam (Oberding, Germany)	10	1125	May	Hesse and Tilting, 1992
Sandy loam (Brockhausen, Germany)	29	1125	April	Hesse and Tilting, 1992
Sandy loam (Dielsdorf, Switzerland)	43	1130	June	von der Mühll *et al*., 1980
Loamy sand (Birkenheide, Germany)	approx. 15-30	1125	May	Hesse and Tilting, 1992

In the 1991 and 1992 trials by Hesse and Tilting the parent compound was detected in the top 25 cm of soil at one or more sites, decreasing from maximum levels in the top 10 cm up to 0.6 mg/kg at day 0 to ≤0.1 mg/kg after approximately 363 days. BF 421-2 was detected mainly in the top 10 cm where it did not exceed 0.05 mg/kg (day 0). It did not exceed 0.02 mg/kg in the 10-25 cm layers. Neither compound was detected (<0.01 mg/kg) below 25 cm.

Huber (1979b) applied [^{14}C]fenpropimorph labelled in the morpholine ring to sandy loam soil in beakers at 6 mg/kg. The soil was kept in the laboratory under aerobic conditions in the dark at 22°C and sampled at intervals for 12 months. After methanol extraction and liquid-liquid partition with chloroform, samples were analysed by scintillation counting, LC on alumina, TLC, HPLC, and radio-GLC and/or GLC-MS. The total radioactivity expressed as fenpropimorph decreased from 6.1 mg/kg initially to 3.5 mg/kg after 12 months.

The proportion extracted by methanol decreased from 87% of the TRR to 17.3% in the 12 months. 80% of the methanol extract could be partitioned into chloroform, and the radioactivity due to the parent compound was shown by TLC to decrease from 96% of that in the chloroform extract to 78% during the 12 months, while degradation products increased. The major compounds in the chloroform extract (months 2 and 3 combined), separated by LC and confirmed by MS, were 62.4% parent, 10% BF 421-8, and 6.7% BF 421-10. The half-life was estimated to be about 20 days.

Huber (1980) treated loamy sand and sandy loam soils with morpholine-labelled fenpropimorph at approximately 5.6 mg/kg soil and measured the $^{14}C0_2$ evolved. Within 45 days approximately 9 and 18% of the fenpropimorph was mineralized respectively. Only trace levels (0.2% of the applied radioactivity) of volatile compounds were detected.

In the study by von der Mühll *et al*. (1980) PVC tubes 5.8 cm i.d. × 15 cm long were driven into sandy loam soil in a wheat field and treated at the equivalent of 1.13 kg/ha with fenpropimorph (free amine) labelled at the benzylic carbon of the methylpropyl group. Dissipation, breakdown and leaching were studied during 12 weeks by Soxhlet-extracting soils from different depths with methanol and analysing them by scintillation counting, HPLC, and TLC with radioscanning. Identities were confirmed by MS.

Radioactivity in the top 5 cm decreased from about 77% of that applied after one week to about 30% after 12 weeks. The proportions in the 5-10 and 10-15 cm levels were 2.3 and 0.6% respectively after the first week and ≤1.5% and 0.3% for the rest of the study. HPLC analysis of the top 5 cm showed the parent compound and BF 421-7 (confirmed by MS) to be the predominant residues (see below).

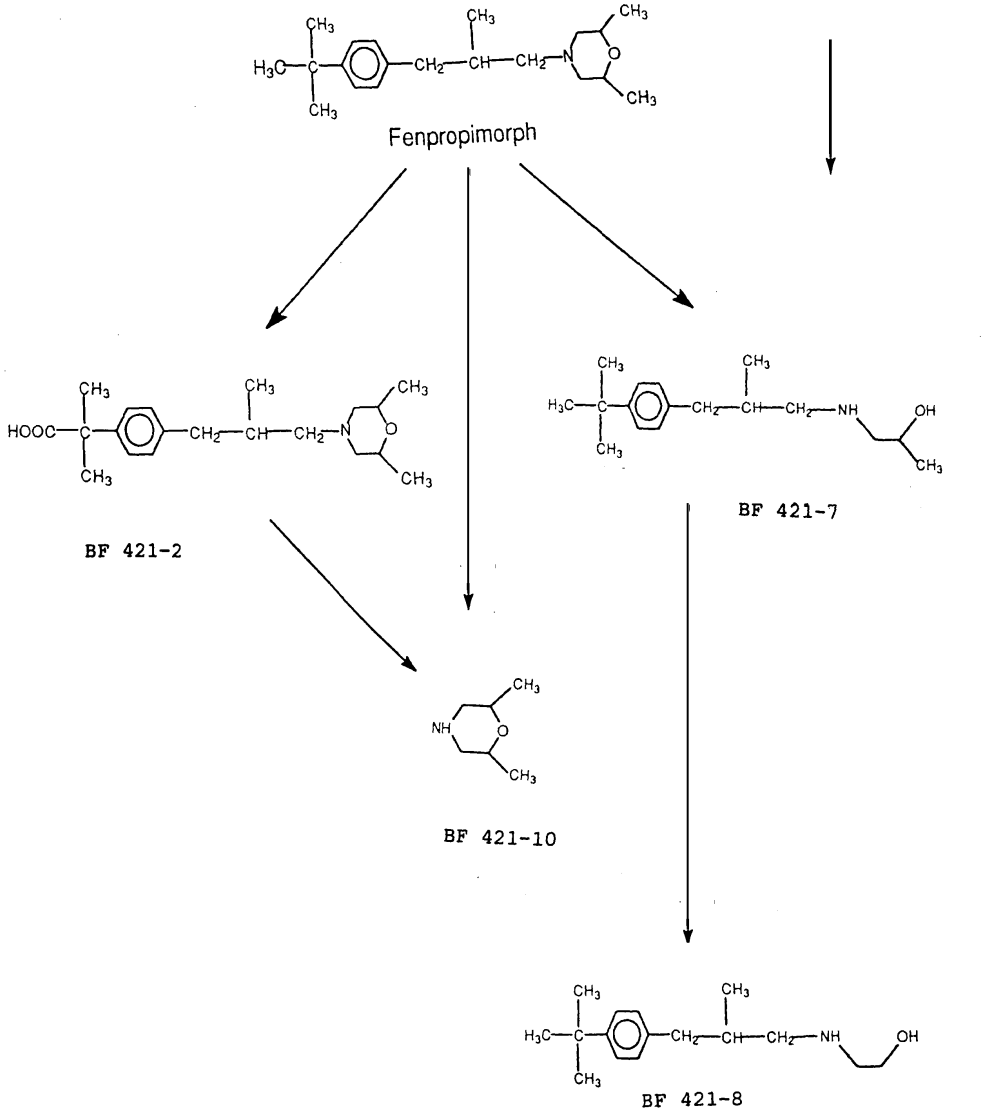
Time	% of applied radioactivity		
(weeks)	fenpropimorph	BF 421-7	Unidentified
1	65	7.8	3.7
2	63	7.5	2.3
4	45	9.8	5.1
8	25	8.1	2.5

12	22	6.1	2.2

In a separate experiment soil was treated at 5.5 mg/kg with [^{14}C]fenpropimorph and incubated at 22°C for 10 weeks. $^{14}CO_2$ was determined for 32 weeks as a measure of the degradation of the parent compound. By the end of the test period a cumulative total of 50% of the applied radioactivity had been evolved as CO_2. No other volatile radioactivity was reported. This was judged to indicate rapid degradation of the parent compound.

The residues identified in soil (Huber, 1979b; von der Mühll *et al.*, 1980) thus include fenpropimorph, BF 421-2, BF 421-7, BF 421-8 and BF 421-10, suggesting the pathways shown in Figure 3.

Figure 3. Degradation pathways of fenpropimorph in soil.



Environmental fate in water/sediment systems

The hydrolysis of fenpropimorph by water (BASF 1982; Rüdel, 1988) is mentioned above in the section on physical and chemical properties. In those studies no hydrolysis products were observed at a neutral pH, although a compound with the TLC characteristics of BF 421-13 was detected at pH 3 and 9. Two laboratory studies on the fate of fenpropimorph in soil/water systems were provided, with the label on the morpholine ring in one (Hamm, 1982) and on the phenyl ring in the other (Ritter, 1990).

In the Hamm study 10-g quantities of a loamy sand at pH 6 (15.7% water = 40% capacity) were treated uniformly in separate conical flasks with 103 ì g of [^{14}C]fenpropimorph labelled in the morpholine ring. The flasks were shaken in the dark at 20°C with 90 ml of a sterile nutrient solution at pH 7 and sampled for analysis at intervals up to 56 days.

After successive extractions with methanol and acid and basic organic solvents, clean-up on an XAD-4 resin column and hydrolysis of some fractions with esterases, samples were examined by scintillation counting, radio-TLC, radio-HPLC, derivatization, and GC-MS (after methylation or acetylation). A control without soil showed no significant degradation by hydrolysis. The production of $^{14}CO_2$ at a level of 11% of the applied radioactivity indicated considerable microbial degradation of the morpholine ring. The half-life was estimated to be about 36 days. The results are shown in Table 13.

Table 13. Degradation of [^{14}C]fenpropimorph in a soil/water suspension (Hamm, 1982).

Days	^{14}C, % of applied					
	Fenpropimorph	Conjugated BF 421-2[1]	BF 421-10	$^{14}CO_2$	Unextracted	Total
0	95.4	0.0	0.0	0.0	4.3	99.7
14	72.7	11.9	1.4	1.2	4.3	91.5
28	40.4	29.4	2.5	3.3	6.8	82.4
56	39.8	28.7	4.2	10.4	6.9	90.0

[1] Hydrolysis of conjugate in methanolic HCl produced methyl ester of BF 421-2. The conjugate was not identified but was probably an ester since its TLC Rf was changed by esterase but not by papainase

In the study by Ritter (following OECD/Swiss GLP) phenyl-labelled fenpropimorph was applied in the laboratory at 0.1 mg/l to natural Rhine river water and pond water (*c*. pH 7.3), each containing 10% of sediment, and incubated for 84 days at 22°C in the dark. Water and soil samples were taken periodically (0, 3, 7, 14, 21, 28, 42 and 84 days) for analysis and CO_2 as well as other volatiles were trapped. Water was extracted with neutral or acidic dichloromethane and soil with methanol for scintillation counting and TLC.

During the 84 days fenpropimorph decreased from 84.2% of the applied radioactivity to 18.2% in the Rhine water system and from 87.1 to 6.8% in the pond water system. Two products were identified and several unidentified compounds were characterized. Representative results in Table 14 show oxidation of the *tert*-butyl group to the alcohol BF 421-1 and acid BF 421-2.

Table 14. ^{14}C residues in Rhine and pond water and sediments after incubation with [^{14}C]fenpropimorph for 84 days (Ritter, 1990).

Compound or fraction	^{14}C, % of applied					
	Rhine (day 3)	Pond (day 3)	Rhine (day 21)	Pond (day 21)	Rhine (day 84)	Pond (day 84)

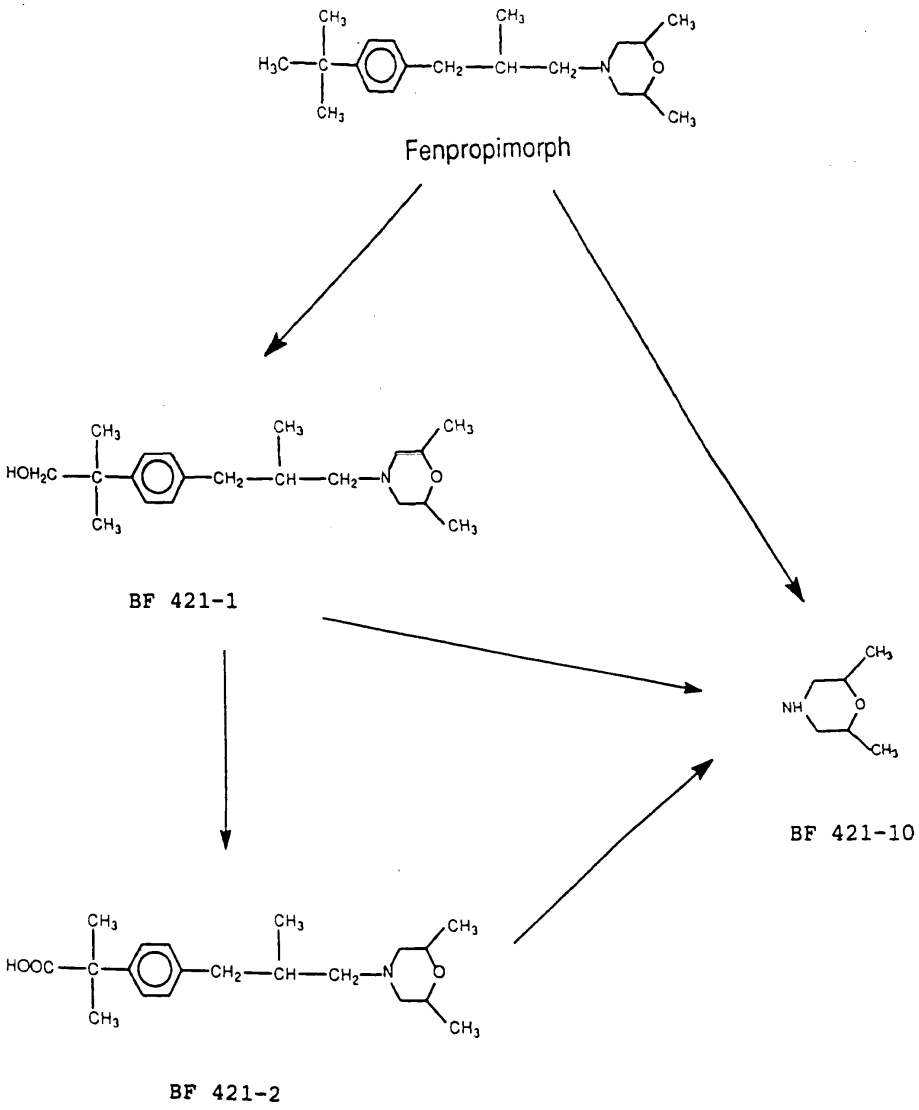
fenpropimorph

	water	soil	water	soil	water	soil	water	soil	water	soil	water	soil
Fenpropimorph	9.6	66	2.8	77	0.8	31	1.0	20	1.2	17	--	5.8
BF 421-1	2.6	--	--	--	--	1.2	--	1.3	--	0.4	--	0.2
BF 421-2	5.5	--	--	--	14.2	3.1	7.7	6.9	13.4	1.7	12.3	0.8
Unknown 1	--	--	--	--	6.6	--	15.1	1.7	--	--	--	--
Unknown 2	--	--	--	--	4.2	--	2.3	--	--	--	--	--
Polar	--	--	--	--	4.5	0.6	4.0	0.7	19.1	1.3	3.6	0.7
Total	18	66	2.8	77	30	36	30.1	30	34	20.4	15.9	7.5

There was 29 and 40% mineralization after 84 days in the Rhine and pond water systems respectively, in which the half-lives of fenpropimorph were 13 and 5 days. Degradation was related to biomass.

The degradation pathways shown in Figure 4 were proposed on the basis of the results of the two studies.

Figure 4. Metabolic Pathways of fenpropimorph in water/soil systems.



METHODS OF RESIDUE ANALYSIS

Analytical methods

Several analytical methods are available for the determination of fenpropimorph in plant materials (mainly cereals and citrus), soil and water, with determination by GLC (usually) or HPLC. A method was also provided for the determination of BF 421-2 in soil. The limits of determination and recoveries for the substrates studied are shown in Table 15.

Plants. Seven methods have been described for the determination of fenpropimorph in plants, five by GLC and two by HPLC. Some are also applicable to soil and water. BASF method 137 (Beutel, 1979) is available for green plants, cereal grains and straws, soil and water. Green plants and straw are chopped with dry ice before extraction with methanol/water; grains are extracted directly. The extracts are concentrated under acidic conditions, partitioned with chloroform, and the concentrated chloroform extract eluted through a cation exchange column with methanol/HCl. The required eluate fraction is partitioned into chloroform, cleaned up on an alumina column, and concentrated. Determination is by GLC with an alkali flame detector. No chromatograms or details of the validations were provided to allow independent confirmation of the limit of determination. The "limit of detection" was reported as 0.05 mg/kg.

BASF method 241 (Beutel and Tilting, 1987) is applicable to cereals, rape, Brassicas, citrus and grapes. Chopped or cut high-moisture samples are added to distilled water and extracted with chloroform for two hours in a Bleidner apparatus. The concentrated extract is cleaned up on a silica gel column (eluted with 2% methanol in methylene chloride), and the eluate concentrated and determined on a packed or capillary column with nitrogen FID detection. Smaller samples are used for low-moisture samples (e.g. straw), and rape and grain samples are macerated in distilled water before the chloroform extraction. Sample chromatograms and other documentation support a limit of determination of 0.05 mg/kg. Detection may be possible at lower levels. Sample chromatograms showed controls to be generally substantially below 0.05 mg/kg.

BASF method 156 (Hänni and von der Mühll, 1981) is also applicable to cereals, soil and water. It is similar to method 241 except that all samples apart from water are macerated before extraction, the extraction is with methylene chloride rather than chloroform, and the alumina column clean-up step is omitted. Controls were <0.05 mg/kg for all samples. The "limit of detection" was reported as 0.05 mg/kg. Limits of determination of 0.05-0.1 mg/kg (0.01 mg/kg for water) appear to be feasible on the basis of the sample chromatograms provided. Detection may be possible at a lower level.

An HPLC method (with confirmation by GLC) has been applied to the determination of fenpropimorph in barley, oats, rye and wheat grains (Zoonen and Harten, 1988). Samples are blended with 5:75 v/v acetonitrile/light petroleum, and to the extract concentrated and partitioned with 1:1 acetonitrile/0.1 N HCl. The aqueous phase is adjusted to pH 9 and extracted with hexane for residue determination. Determination is by HPLC with an ODS stationary phase and a mobile phase of 85:15 acetonitrile/water with 0.25% ammonia. A UV detector at 220 nm is used. Confirmatory analyses are by GLC with alkali flame detection. The reported limits of determination are 0.01 mg/kg for HPLC and 0.005 mg/kg for GLC. The data did not allow confirmation of these levels.

Three methods have been published for determining fenpropimorph specifically in citrus, two by GLC and one by HPLC. In one GLC method (Lafuente *et al*., 1986) citrus samples are chopped, ground and homogenized, and extracted with hexane. The extract is washed with a buffer solution and concentrated, and fenpropimorph is determined by GLC with an NPD. A "limit of detection" of 0.01 mg/kg is reported. On the basis of the limited number of chromatograms available, limits of determination of about 0.1 mg/kg for whole fruit and pulp and 0.2-0.5 mg/kg for peel seem possible.

The other (multi-residue) GLC method is also capable of determining imazalil, prochloraz, propiconazole and thiabendazole (Lafuente and Tadeo, 1987). Whole fruit or peel is homogenized and, after adjustment of the pH, extracted with 90:10 v/v hexane/ethyl acetate. The extract is filtered, concentrated and, without any clean-up, analysed (for fenpropimorph) by GLC with a nitrogen-phosphorus detector. The method is recommended for screening purposes. Although fortification levels were relatively high and few analyses were reported, the "limit of detection" is stated to be 0.1 mg/kg. A limit of determination of 0.2 to 0.5 mg/kg appears to be possible on the basis of the single chromatogram of a control and a sample fortified at 1.8 mg/kg.

The same extraction procedure, without clean-up, is used in the HPLC method (Tadeo and Lafuente, 1987). Determination is by HPLC on an RP-18 stationary phase, with a mobile phase of 87:13 methanol/water plus 0.25% ammonia and UV detection at 215 nm. The limit of "detection" was reported to be 0.03 mg/kg (twice the noise level). The few chromatograms suggest that 0.05 to 0.1 mg/kg may be a feasible limit of determination.

Soil. BASF methods 137 (Beutel, 1979) and 156 (Hänni and von der Mühll, 1981), described above, are applicable to soil. In method 137 dry soil samples are continuously extracted with methanol for 5 hours in a Thiele-Pape or equivalent extractor, and the extract is acidified and concentrated before partition with chloroform. The analysis is completed as described for plant materials. The reported limit of "detection" of 0.05 mg/kg could not be confirmed with the information provided. The limit of determination for method 156 could be estimated to be 0.05 to 0.1 mg/kg for soil. Controls were <0.05 mg/kg.

The simultaneous determination of fenpropimorph and its acid metabolite BF 421-2 in soil has been described by Dieckmann, *et al*. (1993). The method involves extraction with 2:1 acetone/water, liquid/liquid partition with dichlormethane, clean-up by gel permeation chromatography and determination by GLC with an NPD or GC-MS. The acid metabolite is methylated with diazomethane before analysis. Detection limits for GC-MS (electron-impact) were reported as 0.005 mg/kg for fenpropimorph and 0.01 mg/kg for the metabolite. These could not be confirmed nor could limits of determination be estimated from the information available. A single sample chromatogram obtained by GLC with an NPD from soil spiked with 0.4 mg/kg fenpropimorph and 0.04 mg/kg of the acid metabolite as its methyl ester suggests that limits of determination of 0.05-0.1 mg/kg for fenpropimorph and 0.01 to 0.02 mg/kg for the metabolite may be feasible with NP detection.

BASF method 298 (Tilting, 1989) is for BF 421-2 only. Soil samples are extracted with aqueous pH 9 buffer solution, partitioned with dichloromethane and methylated with diazomethane before determination by GLC with NP detection. The buffer does not extract fenpropimorph. The limit of determination is reported as 0.01 mg/kg and sample chromatograms suggest that this level might be achieved, as with the similar method of Dieckmann *et al*.

Water. The general BASF methods 137 and 156 are suitable. Water is acidified before extraction and the analysis is continued as described for plant materials. A limit of detection of 0.05 mg/kg was reported for method 137, but could not be confirmed with the information provided. The limit of determination for method 156 can be conservatively estimated to be 0.01 mg/kg. Controls were <0.01 mg/kg on the evidence of sample chromatograms.

BASF method 271 (Tilting 1987) is specifically for the determination of fenpropimorph in water. Dichloromethane extraction is followed by clean-up on a non-activated silica gel column, concentration and determination by GLC with an NPD, using an internal standard. The reported limit of determination is 0.05 mg/kg. Although sample chromatograms were provided, they were not sufficiently legible for satisfactory confirmation.

Table 15. Analytical methods for fenpropimorph and BF 421-2. All GLC unless shown as HPLC.

Method, ref.	Sample	Limit of determination, mg/kg	Fortification level, mg/kg	Mean recovery, %
BASF 137 (Maag 840-MD-01) Beutel, 1979	Green plants Straws Cereal grains Soil Water	0.05[1]	0.05-5	101 90 86 88 93
BASF 241 Beutel and Tilting, 1987	Wheat forage spindles stalks straw grains Rape forage seeds Brussels sprouts Tangerines Oranges Grapes	0.05	0.05	97 84 86 83 82 76 89 104 94 98 98
Dieckmann *et al*., 1993 (published)	Soil fenpropimorph BF 421-2	 0.05-0.1[2] 0.01-0.02[2]	 0.01-0.1[3]	 99[4] 97[4]
BASF 156 (Maag 840-MD-02) Hänni and von der Mühll, 1981	Green plants Cereal grains Straws Soil Water	0.05-0.1 0.05 0.05-0.1 0.05-0.1 0.01	0.1	88 83 94 74 101
Lafuente and Tadeo, 1987 (published)	Citrus whole fruit peel	 0.2 0.2	 0.6 0.9 0.9 2.3	 96 94 100 89
Lafuente *et al*., 1986 (published)	Citrus whole fruit peel pulp	 0.1 0.2-0.5 0.1	 1 2 0.05	 74 85 74
Tadeo and Lafuente, 1987 (published) HPLC	Citrus whole fruit pulp peel	 0.05-0.1	 1 2 0.05	 74 84 78
BASF 271 Tilting, 1987	Water	0.05 ì g/l	0.05 0.5	88 90
BASF 298 Tilting, 1989	Soil BF 421-2	0.01	0.01	88
Zoonen and Harten, 1988 (submitted for publication) HPLC with GLC confirmation	Cereal grains	0.01 (HPLC)[1] 0.005 (GLC)[1]	0.5	95 90

[1] Reported. Could not be independently confirmed
[2] NPD detection
[3] Only range reported, not individual analyses
[4] MS detection

Stability of pesticide residues in stored analytical samples

The stability of fenpropimorph in ground wheat grain, straw and green plants, and of both fenpropimorph and BF 421-2 in loamy sand, during frozen storage has been investigated by Tilting (1993). Samples spiked at 1 mg/kg with the unlabelled compound(s) were stored in polyethylene bottles in a walk-in freezer up to two years at -20°C. Samples were removed at various intervals for analysis by GLC with nitrogen-FID detection (0.05 mg/kg limit of determination for plant materials and 0.01 mg/kg for soil). Residues of the acid were derivatized with diazomethane before analysis. The proportions remaining were ≥87% except in grain, in which they were 76% ± 21% s.d. The results are shown in Table 16. Those for grain are corrected for the lower and less consistent analytical recoveries.

Table 16. Deep-freeze storage stability of fenpropimorph in wheat and soil and of BF 421-2 in soil after fortification at 1 mg/kg (Tilting, 1993).

Days storage	mg/kg (mean of replicate samples)				
	Fenpropimorph				BF 421-2
	Green plant	Straw	Grain[1]	Soil	Soil
0	0.94	1.1	0.96	0.96	0.91
30-32	0.72	1.1	0.70	0.87	0.86
60-62	0.83	0.95	1.1	0.87	0.70
118-119	0.91	0.89	0.89	0.80	0.83
180	1.0	0.93	0.96	0.72	0.90
242-243	0.71	1.0	0.88	0.79	0.76
362	0.84	1.0	1.0	0.89	0.78
735-742	0.96	0.99	0.93	0.93	0.82

[1] Corrected for analytical recoveries

Residue Definition

In plant metabolism studies fenpropimorph was shown to be by far the predominant residue shortly after application and even at harvest it is typically at least three times the level of any identified metabolite. A possible exception in some circumstances is the metabolite BF 421-7 (the hydroxypropyl amine) which was shown in one study, but not in another, to occur at about the same level as the parent compound. For enforcement purposes fenpropimorph *per se* is therefore the appropriate definition of the residue in plants. If worst-case assumptions are needed for risk assessment purposes, it might be argued from the metabolism studies that total residues of the parent plus identified metabolites in plants could be as much as three times those of fenpropimorph alone, but the preponderance of the evidence suggests that no more than half that ratio is likely.

Metabolism studies have not shown unchanged fenpropimorph in goats or hens except in hen kidneys. If the residue in animal products is to be defined, residue data would be needed for the metabolites BF 421-1, BF 421-2 and BF 421-3, the predominant residues identified in goats and hens.

USE PATTERN

Fenpropimorph is registered in over 30 countries (mostly in Western Europe), mainly in cereals for the control of powdery mildew, rust and (in barley) leaf blotch. The EC is reported to be the most widely used formulation. Many of the products are mixed formulations with other active ingredients. GAP relevant to the residue data provided for cereals is shown in Table 17 and includes information from the manufacturer and governments. It refers only to fenpropimorph, although in some cases the formulation might be mixed. GAP for crops other than cereals on which residue trials were reported is shown in Table 18.

Table 17. GAP for field uses of fenpropimorph on cereals.

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
Cereals						
Austria	EC	0.75	0.13-0.25	1-2	35	
Norway	EC	0.75	0.38	1*	28	stage 59 * country submission states 1-2 applic. to "corn"; stage 59
Spain	EC	0.75	≤0.38	1-2	35	stage P
Sweden	EC	0.19-0.75	0.1-0.38	1-3	--	stage P, stage 59
Saudi Arabia	EC	0.75	0.19	1		
UK	EC	0.75		3	35	
Barley						
Austria	EC	0.75	0.15-0.38	1-2	35	
Belgium	EC/SC/SE	0.33-0.75	0.09-0.25	1-2	28-42	at last leaf beard or knot; 14 days not confirmed
Belorussia	EC	0.2-0.3		1-2	--	stage 29-37
Croatia	EC	0.75		1	42	
Czech Republic	EC	0.75		1	42	
France	EC/SC/SE	0.26-0.75	0.19-0.75	1-2--	--	1-2 nodes
Germany	EC	0.42-0.75	0.12-0.14	1-2	35	at infection; stage 29-61
Greece	EC	0.75	0.15	2	30	at flowering
Ireland	EC	0.38-0.56	0.12-0.28	2-3	35	stages GS 32, 59, 71
Italy	EC	0.75	0.15	1-2	35	at infection; blooming
Kasakstan	EC	0.2-0.3	--	1-2	--	
Luxembourg	EC/SC/SE	0.38-0.75	0.1-0.25	1-2	42	last leaf beard, first knot
Netherlands	EC	0.75	0.19	1-2	42	DC 39, 59 stage
New Zealand	EC	0.38-0.75	0.19-0.38* 0.38-1.5**	1-2	42	*ground **aerial at disease/ear emergence
Norway	EC/SC	0.6-0.75		1	--	
Poland	EC	0.75		1	--	
Portugal	EC	0.75	0.08	1-2	35	stage 31-Z
Rumania	EC	0.3-0.75	0.15-0.3	1-2	--	stage 21-55, 29-37, 51-59
Russia	EC	0.2-0.3	--	1-2	--	
Serbia	EC	0.75		1	42	

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
Slovakia	EC	0.75		1	42	
Slovenia	EC	0.3-0.75	0.08-0.15	1-2	42	stage 37-49
Spain	EC	0.75		--	35	at infection
Switzerland	EC/SC	0.38-0.75	0.06-0.12	1	--	stage 31-51
UK	EC	0.3-0.75	0.08-0.38	1-3	35	at disease; ≥3 months autumn/spring to summer applic.
Uruguay	EC	0.75	--	1-2	35	
Yugoslavia	EC	0.75		1	42	
Summer Barley						
Belgium	SE/SC	0.8		1-2	28	
Belorussia	EC	0.75		2	--	vegetative stage
Denmark	EC	0.75		1-2	30	
Netherlands	EC	0.75	0.13-0.38	1	42	NL submission. Tillering till 1st ears
Russia	EC	0.75		2	--	vegetative period
UK	EC	0.5		1-2	35	
Ukraine	EC	0.75		2	--	vegetative period
Spring Barley						
Denmark	EC	03-0.75	0.15-0.38	1-2	30	stage 39-49
UK	EC	0.38-0.75		2	35	UK submission, early milk stage; including ear emergence; ≥3 months autumn/spring-summer applic.
Winter Barley						
Belgium	SC	0.8		1	28	
Belorussia	EC	0.75		2	--	vegetative stage
Denmark	EC	0.3-0.75	0.15-0.38	1-2	30	stage 59
Germany	EC	0.75		2	35	at infection
Netherlands	EC	0.75	0.13-0.28	1-2	42	NL submission, at infestation; tillering till 1st ear
Russia	EC	0.75		2	--	vegetative period
UK	EC	0.5-0.75		2-3	35	max. 2 applic. Jan. 1-harvest; before early milk stage, including ear emergence
Ukraine	EC	0.75		2	--	vegetative period
Oats						
Austria	EC	0.75	0.15-0.38	1-2	35	
Belgium	EC/SC	0.38-0.80	0.09-0.25	1	28-42	at or before infection
Ireland	EC	0.38-0.56	0.19-0.28	3	35	stage 71
Italy	EC	0.75	0.15	1-2	35	at infection; start of blooming
Luxembourg	EC	0.38	0.1-0.25	1	42	totally visible ear
Netherlands	EC	0.75	0.13-0.38	1-2	42	NL submission; at infestation; DC 39, 59
Portugal	EC	0.75	0.08	1-2	35	stage 31-Z

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
UK	SC	0.75	--	1	35 52*	*before flowering; UK submission
UK	SC	0.56	--	2	35 56*	*before flowering; UK submission
UK	EC	0.38-0.5	--	3	35	UK submission. Lower rate ≥3 months between autumn/spring and summer applic.
UK	EC	0.75	0.38	1-2	35	UK submission
Spring Oats						
UK	EC	0.75		2	35	UK submission
Summer Oats						
Luxembourg	SE	0.8		2	42	
Winter Oats						
Luxembourg	SE	0.8		2	42	
UK	EC	0.75		3	35	UK submission. Max. 2 applic. Jan. 1-harvest
Rye						
Austria	EC	0.75	0.15-0.38	1.2	35	
Belgium	SE	0.35		1-2	42	
Czech Republic	EC	0.75		1	42	
Denmark	EC	0.3-0.75	0.15-0.38	1-2	30	stage 39
Germany	EC	0.50.75	0.11-0.14	1-2	35	stage 29-51
Italy	EC	0.75	0.15	1-2	35	at infection; start of blooming
Poland	EC	0.75		1	--	
Slovakia	EC	0.75		1	42	
Switzerland	EC	0.38		1	--	stage 39-61
UK	EC	0.75	0.38	1-2	35	at disease; including ear emergence, before early milk
UK	EC	0.38-0.5	--	3	35	≥3 months between autumn/spring-summer applic. UK submission
UK	SC	0.56	--	2	35	UK submission
UK	SC	0.75	--	1	35	UK submission
Uruguay	EC	0.75		1-2	35	
Winter Rye						
Belorussia	EC	0.75		2	--	
Russia	EC	0.75		2	--	vegetative period
UK	EC	0.66		2	35	
Ukraine	EC	0.75		2	--	vegetative period
Summer Rye						
Belorussia	EC	0.75		2	--	vegetative period
Russia	EC	0.75		2	--	vegetative period
Ukraine	EC	0.75		2	--	vegetative period

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
Wheat						
Austria	EC	0.75	0.15-0.38	1-2	35	
Belgium	EC/SC	0.38-0.75	0.1-0. 25	1-2	14-42	stage 1/L/M; 14 days not confirmed (label states 4 wks. for cereals)
Belorussia	EC	0.2-0.3		1-2	--	stage 29-37, 51-59
Brazil	EC	0.5-0.93		1-2	35	at first disease
France	EC/SC/WP	0.35-0.75	0.12-0.75	1-2	--	1-2 node stage
Germany	EC	0.5-0.56	0.11-0.14	1-2	35	stage 29-61
Greece	EC	0.75	0.15	2	30	ear appearance
Ireland	EC	0.38-0.56	0.12-0.28	2-3	35	stages 32, 71
Italy	EC/SC/NP	0.75	0.15-0.5	1-2	35	start of blooming
Kasakstan	EC	0.2-0.3	--	1-2		
Luxembourg	EC	0.38-0.75	0.1-0.25	1-2	14-42	totally visible ear
Netherlands	EC	0.75	0.1-0.38	1	42	DC 39, 59; development of first ear till blossom
New Zealand	EC	0.38-0.75	0.19-0.38* 0.38-1.5**	1-2	42	*ground **aerial at disease/ear emergence
Poland	EC	0.75		1	--	
Portugal	EC	0.75	0.08	1-2	35	stage 31Z
Rumania	EC	0.3-0.75	0.15-0.3	1-2	--	stage 21-55, 29-37, 51-59
Russia	EC	0.24-0.3		1-2	--	stage 29-37, 51-59
Slovenia	EC	0.3	0.08-0.15	1-2	--	stage 37-49
Spain	EC	0.75		--	--	before flowering; Spanish submission
Switzerland	EC/SC	0.38-0.75	0.06-0.25	1-2	--	stages 30-32, 30-39, 30-61, 31-32, 29-39, 31-39. 37-61, 37-61, 51-61
UK	EC	0.3-0.75	0.08-0.38	1-3	35	at disease
Spring wheat						
UK	EC	0.38-0.56		2	35	including ear emergence; ≥3 months autumn/spring-summer applic.
Summer Wheat						
Belgium	SC/SE	0.38-0.8		1-2	28	
Belorussia	EC	0.75		2	--	vegetative period
Luxembourg	SE	0.6		2	42	
Netherlands	EC	0.5-0.75	0.08-0.25 for 0.5 kg/ha 0.1-0.38 for 0.75 kg/ha	1-2	42	up to blooming; till first ears visible
Russia	EC	0.75		2	--	vegetative period
Ukraine	EC	0.75		2	--	vegetative period
Winter Wheat						
Belgium	SC/EC/SE	0.38-0.8		1-2	28-42	42 days for SE or EC; till ear forming for EC
Belorussia	EC	0.75		2	--	vegetative period

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
Denmark	EC	0.38-0.75	0.19-0.38	1-2	30	stage 59
Hungary	EC	0.75	0.15-0.3	1-2	42	stage 21-55
Netherlands	EC	0.5-0.75	0.1-0.38 h. rate	1-2	42	first ears till blooming
Luxembourg	SC/SE	0.6-0.75		2	--	
Russia	EC	0.75		2	--	vegetative period
UK	EC/SC	0.5-0.75		1-3	35	at infection; including ear emergence, before milk; max. 2 applic. Jan. 1-harvest; ≥3 months autumn/spring-summer applic.
Ukraine	EC	0.75		2	--	vegetative period
Soft Wheat						
Belgium	SC	0.6		1	28-42	
Bulgaria	EC	0.75		1	--	
Croatia	EC	0.75		1	42	
Czech Republic	EC	0.75		1	42	
Denmark	EC	0.75		1-2	30	
France	EC/SC/SE	0.28-0.75		--	--	
Germany	EC	0.75		2	35	
Greece	EC	0.75		2	30	at flowering
Italy	EC	0.75		2	35	at infection
Luxembourg	SC	0.8		1	--	
Netherlands	EC/SC	0.6-0.75		3	42	1 day for SC
Norway	SC	0.6		1	--	
Poland	EC	0.75		1	--	
Serbia	EC	0.75		1	42	
Slovakia	EC	0.75		1	42	
Slovenia	EC	0.75		1	42	
Spain	EC	0.75		--	35	at infection
Taiwan	EC	0.30	--	2	14	
Uruguay	EC	0.75	--	1-2	35	
Yugoslavia	EC	0.75		1	42	

Table 18. GAP for the use of fenpropimorph on beans, carrots, leeks and sugar beet,

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
Beans						
UK (incl. field beans)	EC	0.75	0.19-0.38	1-2	35	at disease
Carrots						

Crop, country	Application				PHI, days	Notes (Growth stage of application etc.)
	Form.	Rate		No.		
		kg ai/ha	kg ai/hl			
UK	EC	0.75		3	28	UK submission
Leeks						
Belgium	EC	0.75			21	at disease
Denmark	EC	0.56-0.75	0.28-0.38	1-2	28	max 1/yr.; leaves not to be used as fodder
Luxembourg	EC	0.75		--	21	at disease
Netherlands	EC	0.75	0.12-0.19	2-4	21	Autumn
UK	EC	0.75	0.19-0.38	1-6	21	at disease; 14 day interval
Sugar beet						
Belgium	EC SC[1]	0.56 0.56		-- 1	-- 28	at disease
Denmark ("beet")	EC	0.56-0.75	0.28-0.38	1-2	28	before Sept.; max 1/yr., leaves not to be used as fodder
France ("beets")	EC	0.75		--	--	
Greece sugar beet "beet"	EC EC	0.5-1.1 0.75-1.1	-- 0.15-0.25	1 2	7 7	at flowering 1-2 month pre-harvest
Luxembourg	EC	0.56		--		at disease
Switzerland	EC[2]/EC[3]	0.30-0.38	0.06-0.13	1	--	at symptoms

[1] 375 g fenpropimorph + 125 g carbendazim/l product
[2] 375 g fenpropimorph + 125 g propiconazole/l product
[3] 187 g fenpropimorph + 250 g chlorothalonil + 80 g flusilazole/l product

RESIDUES RESULTING FROM SUPERVISED TRIALS

In plants

Results of residue trials were available for cereals, beans, leeks, and sugar beet (Ciba, 1994). Summary reports of supervised trials were also received from Norway on barley, onions, wheat, oats and carrots (Race, 1994). In the absence of the detailed data these reports were not reviewed by the Meeting.

In Tables 19-22 underlined residues are from treatments according to or approximating GAP.

Cereals. About 300 reports of supervised trials were available for barley, oats, rye, and wheat, mainly in Western Europe. The results are shown in Tables 19 (barley, 102 reports), 20 (oats and rye, 17 reports), and 21 (wheat, about 180 reports).

Table 19. Supervised trials with fenpropimorph on barley.

Country, year, (variety)	Application*				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Green plant or whole plant	
Barley									
Belgium 1980, 2 sites	EC	1	0.75		71 76 controls	<0.08 <0.08 <0.08			81/046

Country, year, (variety)	Application*				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Green plant or whole plant	
France 1979	EC	2	0.75		48 controls	<0.05 <0.05	0.2 0.1		79035
Germany 1989	EC	2	0.56 3/4 × max	0.14	0 21 35 controls	-- 0.6 (E) 0.09 <0.05	-- -- 1.1 <0.05	2.4 -- -- <0.05	89085
Germany	EC	2	0.56	0.14	0 -- 36 50 controls	-- 0.1 (E) 0.08 <0.05 <0.05	-- -- 0.2 0.4 <0.05	4.4 -- -- -- <0.05	89086
New Zealand 1983	EC	2	0.75 1.5		53 53 controls	0.4 0.5 <0.05	0.6 1.1 <0.05		83033
New Zealand 1984 (Triumph)	EC	2	0.75 1.5		66 66 controls	<0.05 <0.05 <0.05	-- -- --		84036
New Zealand 1984 (Gold-maker)	EC	2	0.75 1.5		61 61	0.07 0.15	-- --		84037
New Zealand 1984 (Triumph)	EC	2	0.75 1.5		62 62	<0.05 <0.05	-- --		84038
Sweden 1981 (Mona)	EC	1	0.75	0.19	69	<0.05	0.3		82064/c
Sweden 1980[2] 2 varieties each rate	EC	1	0.75 2.3		36 36 controls	0.09 (2) 0.4, 0.2 <0.05	0.9, 1.2 2.9, 3.4 0.3		80058

Spring barley									
Denmark 1982	EC	1	0.38	0.19	36 75-88 controls	<0.05 (2) <0.05	0.4 (2) 0.05	0.2(2) 0.05	82082, 82083, 82103-4
Denmark 1979-80 7 sites	EC	1	0.75		74-97 controls	<0.05 (7) <0.05	<0.05 (2) 0.06 (2) 0.07 0.12 <0.05		79069, 80094-7
Denmark 1979 3 sites	EC	1	1.1		74-86 controls	<0.05 (3) <0.05	<0.05, 0.07, 0.09 <0.05		79069
Denmark 1980	EC	1	0.75	0.19	30	0.2	0.2		42100F-80/24E
Denmark 1982	SC[3,4]	1	0.6	0.15	84	<0.05	0.2		43805F-82/1E
Denmark 1990	EC[5]	2	0.38	0.19	0 20-21 34-35 55-65 controls	 <0.02(2), 0.02 <0.02-0.04	 0.04, 0.08(2) 0.02	5(2), 7 0.1(2) 0.05, 0.1, 0.06 -- 0.02-0.1	2145/91 2148/91 2150/91
Denmark 1990	EC[5]	1	0.38	0.19	25-26 39-40 61-70 controls	 <0.02(3) <0.02-0.04	 0.04, 0.06, 0.05 0.02-0.03	0.08, 0.09, 0.1 0.04, 0.05, 0.09 -- 0.02	2146/91 2149/91 2151/91
Denmark 1990	EC[5]	1	0.75	0.38	26 40 70 controls	 <0.02 <0.02	 0.05 0.02	0.13 0.06 -- 0.02	2147/91
Finland 1981	EC	1	0.56	0.26	52	<0.05			3278/81
France 1979	EC	1	0.75		71 control	<0.05 <0.05	0.05 <0.05		79028
France 1979	EC	2	0.75	0.15	53 controls	<0.05 <0.05	0.5 <0.05		79041
France 1979	EC	2	0.75		43 controls	0.08 <0.05	0.14 <0.05		79048
France 1978	EC	1	1.1	0.19	79	<0.05	0.31		42100F-78/10E
France 1979 3 trials	EC	1	0.75	0.13	55-75	<0.05 (3)	0.9, 0.2, 0.5		79/3E, 79/4E, 79/5E
Germany 1980	EC	1	0.75	0.13	0 14 21 28 35	 <0.05	 1.8	14 0.6 0.5 0.6 --	42100F-80/6A
Germany 1980	EC	2	0.75	0.13	0 14 21 28 35	 2.5 0.1	 1 0.3	11 0.6 0.4 -- --	42100F-80/5A
Germany 1980	EC	2	0.75	0.13	0 21			20 0.4	-80/7A

					28 35 42	 0.1 0.07	 0.7 1.3	0.3 -- --	
Germany 1980	EC	2	0.75	0.13	0 14 21 28 35 44	 0.2 0.06 <0.05	 0.5 0.8 0.7	8 0.7 0.7 -- -- --	-80/8A
Germany 1980	EC	2	0.75	0.13	0 14 21 28 35	 0.1 0.1	 0.9 1.3	27 0.8 0.6 -- --	-80/9A
Germany 1982	SC[3,4]	1	0.6	0.1	0 21 28 35 42	 <0.05 <0.05	 0.3 0.4	13 <0.1 <0.1 -- --	43805F-82/7A
Germany 1988	EC[6]	2	0.56	0.14	0 21 28 35 42	 0.3 (E) 0.3(E) 0.1 0.1	 1.8 1.4	6.1 1.2 (stalk) 0.9 (stalk)	-88/5A
Netherlands	EC	1	0.75 1.1 1.5		70 70 70 controls	<0.05 <0.05 <0.05 <0.05	<0.05 0.08 0.06 <0.05		79082
Sweden 1982	SC[3,4]	1	0.6	0.13	55-79	<0.05 (6)			43805F82 /1E, /2E, /3E, 4E, /5E, /6E
Sweden 1983	SE[3,4]	1	0.6 0.8X	0.25	50-74	0.1, 0.2(3)			43805F 83/1E-4E
Sweden 1983	SE[3,4]	2	0.6	0.25	36 51 58	0.2 0.1 0.2, 0.4			-83/5E-8E
UK 1979	EC	 2 1	 0.75 1.1 1.1 1.1	 0.36 0.53	(GAP=30) 29 29 29 71 controls	 0.2, 0.2 0.2, 0.3 0.2, 0.3 <0.05 (2) <0.05	 0.6, 0.8 1.2, 1.1 0.6, 0.9 0.5, 0.6 0.14		79052
UK 1979	EC	2 1	0.75 1.1 1.1 1.1	0.36 0.53 0.53	32 32 32 74 controls	0.08, 0.09 0.09, 0.1 0.1 (2) <0.05 (2) <0.05	0.3, 0.8 0.2, 0.7 0.14, 0.2 0.1, 0.2 0.3		79053
UK 1979	EC	1	1.1	0.45	65-82	<0.05 (5)	<0.05 (4) 0.4		42100F-78/1E, /2E, /3E, /8E, /9E
UK 1979	EC	1	0.75	0.3	0 7 14 21 75	 <0.05	 1.2	27 7.3 2.6 2 --	42100F-79/13 A
UK 1979	EC	1	1.1	0.56	29 32 63	0.13 0.08 <0.05	2.5 1.3 1.5		42100F-79/29E, /32E, /33E

UK 1979	EC	2	0.75	0.3	28 77	<0.05	1.3	1.8	42100F- 79/11A
UK 1979	EC	2	0.75	0.3	28 43 48	<0.05	2.2	1.1	-79/12A
UK 1986	EC	1	1.5	0.63	62	0.09 0.06 **malt**			42100F-87/9E
Winter Barley									
Denmark 1980	EC	1	0.75	0.19	(GAP=30) 67 79	<0.05 <0.05	0.6 0.1		42100F- 80/19A
Denmark 1980	EC	1	0.56 0.75		67 53 67 control	<0.05 <0.05 <0.05 <0.05	0.4 0.5 0.6 --		80098
Denmark 1983 2 trials	SC[3,4]	1	0.6	0.15	31-32 62-63 76-77	<0.05(2)(E) <0.05(2)	0.2 0.1, 0.3	<0.1, 0.2	4305F-83/1A, /2A
France 1979	EC	2	0.75 1.1	0.15 0.23	60 60 control	<0.05 <0.05 <0.05	0.3 0.4 <0.05		79034
France 1979 2 trials	EC	2	0.75		64[7] control	<0.05 <0.05 <0.05	0.06 0.07 <0.05		79036
France 1978	EC	1	1.1	0.19	75-79	<0.05(2)	<0.05, 0.08		42100F 78/16-17
France 1979 3 trials	EC	1	0.75	0.13	49 88 91	<0.05 <0.05 <0.05	1 0.1 0.09		-79/1E, /2E, /6E
Germany 1987	EC	2	0.4	0.2	0 15 28 35 42 controls	16 (E) 0.1 (E) 0.05 (E) 0.07 <0.05 <0.05 (grain & E)	0.2 0.3 <0.05		87070
Germany 1981	EC	3	0.75	0.13	0 21 28 35 42	0.8(E) 0.6(E) 0.3[8] 0.3[8]	9.8 5.9 4.8[8] 4.2[8]	31	42100F81/1A
Germany 1981	EC	3	0.75	0.13	0 21 28 35 42 56	0.2 (E) 0.1 (E) 0.09 (E) <0.05[8]	0.5 1.5[8] 0.7[8] 0.6[8]	9.6 1.7	-81/2A
Germany 1981	EC	3	0.75	0.13	0 21 28 35 42 controls	0.4 (E) 0.4 (E) 0.5 (E) 0.1[8] <0.05	1.4[8] <0.1	13 2.3 (stalk) 2.2 (stalk) 1.8 (stalk) <0.1	-81/5A
Germany 1981	EC	3	0.75	0.13	0 21 28	0.4(E) 0.3(E)	1.1 1.3	14	-81/6A

					35 38/42 controls	0.3(E) 0.1[8](2) <0.05	1[8] 0.7[8](2) <0.1	<0.1	
Germany 1981	EC	3	0.75	0.13	8 21 28 31 35 42 controls	1.2(E) 0.7(E) 0.2 0.2 0.2[8] 0.1[8] <0.05	1.6 1.6 2.6 2.1 1.8[8] 1.8[8] <0.1		-81/7A
Germany 1982	SC[3,4]	1	0.6	0.1	0 21 28 35 42 50 controls	 0.2(E) 0.06 <0.05 <0.05	 0.8 0.9 <0.1	7 0.6 0.3	43805-82/5A
Germany 1982	SC[3,4]	1	0.6	0.15	0 21 28 35 42 49 controls	 0.05 0.07 <0.05	 1.3 <0.1 <0.1	6 0.3 0.4 0.2	-82/6A
Germany 1988	EC[6]	2	0.56	0.19	0 21 28 35	 0.3(E) 0.2	 0.6	11 0.5 0.8 (stalk)	46400F-88/1A
Netherlands 1979	EC	1 2	0.56 0.75		61 40 controls	<0.05 <0.05 <0.05	0.08 0.1 <0.05		79081
Netherlands 1979	EC	2	0.56 0.75		46 46 controls	0.05 0.06 <0.05	0.1 0.1 <0.05		80079
Switzerland 1979	EC	2 (GAP=1)	0.75		0 14 28 42 49 control	 <0.05 <0.05	 0.06 <0.05	8.2 0.2 0.09 0.07 0.06 <0.05	79014
UK 1979	EC	1	0.75 1.1		55 55 controls	0.05, 0.12 0.07, 0.14 <0.05	0.06, 0.16 0.2, 0.12 <0.05		79042
UK 1979	EC	1	0.75 1.1		35 35 controls	0.1 (2) 0.2 (2) <0.05	0.6, 1.1 0.9 (2) <0.05		79044
UK 1979 2 trials	EC	1	1.1	0.5	37 48	0.07 <0.05	1.9 1.6		42100F-79/17A
UK 1979 2 trials	EC	1	1.1	0.56	35 57	0.09 <0.05	1.1 1		-79/35E, 36E

* kg ai/ha or /hl for mixed formulations refers only to fenpropimorph
[1] Numbers in parentheses = no. of samples with that residue
[2] Only 4m^2 plot. Plots in most other trials were ≥40m^2
[3] 200 g fenpropimorph, 330 g chlorothalonil/1 product
[4] GAP is for EC formulations
[5] 375 g fenpropimorph, 225 g prochloraz/1 product
[6] 563 g fenpropimorph, 187 g tridemorph/1 product
[7] Harvest to analysis 3 years. No data on storage conditions or analytical method

[8] Referred to UK GAP which allows up to 3 applications. German allows 2

Table 20. Supervised trials with fenpropimorph on oats and rye.

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Green plant or whole plant	
Oats									
UK 1980	EC	2	0.75	0.38	38 49 83	 <0.05	 1.2	1.1 0.5	42100F-80/12A
UK 1980	EC	2	0.75	0.38	35	0.4	0.8		-80/2E
UK 1980	EC	2	0.75	0.38	81	<0.05			-80/3E
Rye									
Germany 1989	EC[2]	2	0.56	0.14	0 21 35 42 controls	 0.4(E) <0.05 <0.05 <0.05	 0.3 0.3 <0.05	2.7	89083
Germany 1989	EC[2]	2	0.56	0.14	0 22 42 49 controls	 0.3(E) 0.1 0.09 <0.05	 0.4 0.2 <0.05	3.8 <0.05	89084
Sweden 1980	EC	1	0.75		--	<0.05			80069
Sweden 1984 4 trials	SC[3]	1	0.75	0.19	95-111	<0.05(4)			43102F-84/5E, 6E, 7E, 8E
Sweden 1983 2 trials	SC[3]	2	0.75	0.19	82	0.3, 0.4			43102F-83/5E, -83/6E
UK 1983 aerial	EC	2	0.75	1.7	45	<0.05	1		42100F-83/1E
UK 1983	EC	2	0.75	0.34	49	<0.05	1.3		-83/2E
Winter rye									
Sweden 1980	EC	1	0.75		-- controls	<0.05 <0.05	0.09 <0.05		80067
Sweden 1981	EC	1	0.75	0.19	107 controls	<0.05 <0.05	0.05 <0.05		82064/a
Sweden 1981	EC	1	0.75	0.19	80 controls	<0.05 <0.05	0.6 <0.05		82064/b

[1] Numbers in parentheses = no. of samples with that residue
[2] 281 g fenpropimorph, 200 g prochloraz/1 product
[3] 375 g fenpropimorph, 125 g carbendazim/1 product

Table 21. Supervised trials with fenpropimorph on wheat.

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
Wheat									
Belgium 1980	EC	1	0.75		66	<0.08 <0.08			81/047
France 1979	EC	1	0.75		71 controls	<0.05(2)	0.05, 0.06		79037
France 1984 5 trials	WP[2]	2	0.66	0.13	58-90 controls	<0.05(5) <0.05			84112, -13, -14, -15, -16
Greece 1986 (Vergina & Egis)	EC	2	0.75	0.19	56 controls	<0.05(2)			86208, 86209
Italy 1982 (Creso & Irnerio) 2 trials	EC	1 1 2	0.75 0.75 0.75		81-88 38-39 38-39 controls	<0.05(4) <0.05(4) <0.05(4) <0.05	0.1(2), 0.2(2) 1.6, 1.9 1.1, 2.2 1.9, 2.3, 1.9, 1.8 0.07		82084, 82085
New Zealand 1983 3 trials	EC	2	0.75 1.5		48-52 controls	<0.05(3) <0.05(3) <0.05	2.4, 2.1 4.5, 4.3 0.2		83032/a, /b, /c
Switzerland 1980	EC	2	0.75		52 56	<0.05	0.7	0.9	80031
Spring wheat									
France 1978	EC	1	1.1	0.19	48	<0.05	0.3		42100F- 78/11E
France 1978	EC	1	1.1	0.19	76	<0.05	<0.05		-78/12E
France 1978	EC	1	0.75	0.13	32	<0.05	0.9		-79/7E
France 1979	EC	1	0.75	0.13	70	<0.05	0.5		-79/11E
Germany 1977	EC	1	0.75	0.13	0 28 35 42 49 56 63	 <0.05 <0.05	 0.1 0.08	10 1.1 0.4 0.3 0.1	42100F- 77/1A
Germany 1977	EC	1	0.75	0.13	0 28 35 42 49 56 63	 <0.05 <0.05 <0.05	 0.2 <0.05 <0.05	14 0.1 0.1 0.05	-77/2A
Germany 1977	EC	1	0.75	0.13	0 28 35 42			17 0.8 0.3 0.1	-77/3A

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					49			<0.05	
					56	<0.05	0.08		
					63	<0.05	0.07		
					70	<0.05	0.07		
Germany 1977	EC	1	0.75	0.13	0			8.6	-77/4A
					28			0.2	
					35			0.2	
					42			0.08	
					49			0.1	
					56		0.09		
					63	<0.05	0.07		
Germany 1977	EC	1	0.75	0.13	0			7.8	-77/8A
					21			0.8	
					28			0.4	
					35			0.4	
					42	<0.05	0.2		
					49	<0.05	0.1		
					56	<0.05	0.1		
Germany 1977	EC	2	0.75	0.13	0			7.3	-77/5A
					21			0.5	
					28			0.4	
					35			0.3	
					42	<0.05	0.3		
					49	<0.05	0.2		
					56	<0.05	0.2		
Germany 1977	EC	2	0.75	0.13	0			17	-77/6A
					21			1.4	
					28			0.4	
					35			0.3	
					42			0.2	
					49	<0.05	0.1		
					56	<0.05	0.1		
					63	--	0.1		
Germany 1977	EC	2	0.75	0.13	0			11	-77/7A
					21			0.3	
					28			0.3	
					35	0.07	0.2		
					42	<0.05	0.2		
					49	<0.05	0.06		
					56	<0.05	0.06		
Germany 1978	EC	2	0.75	0.13	0			15	-78/1A
					21			1.1	
					28			0.6	
					35			0.4	
					42			0.3	
					49	<0.05	0.2		
					56	<0.05	0.2		
					63	<0.05	0.2		
Germany 1978	EC	2	0.75	0.13	0			15	-78/2A
					21			0.2	
					28			0.08	
					35			0.08	
					42			<0.05	
					49	<0.05	0.08		

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					56	<0.05	0.1		
Germany 1978	EC	2	0.75	0.13	0 21 28 35 42 49 56 63	 <0.05 <0.05	 0.05 <0.05	8.1 0.4 0.3 0.2 0.07 0.06	-78/3A
Germany 1978	EC	2	0.75	0.13	0 21 28 35 42 49 56	 <0.05 <0.05 <0.05	 0.4 0.3	17 1 0.6 0.5	-78/4A
Germany 1978	EC	1	1.1	0.19	0 21 28 35 42 49 56	 <0.05 <0.05 <0.05	 0.2 0.08 0.07	17 0.5 0.3 0.3	-78/5A
Germany 1978	EC	1	1.1	0.19	0 21 28 35 42 49 56 63	 <0.05 <0.05 <0.05	 0.1 0.1 0.2	23 0.5 0.2 0.2 0.1	-78/6A
Germany 1979	EC	2	0.75	0.13	0 14 21 28 35	 <0.08 <0.08	 <3.6 <3.6	14 2.2 1.6	42100F-79/1A
Germany 1979	EC	2	0.75	0.13	0 14 21 28	 <0.12	 <1.6	6.9 2.5 1.8	-79/2A
Germany 1979	EC	2	0.75	0.13	0 14 21 28 35 42	 <0.05 <0.05 <0.05	 <1.9 <1.6 <1.6	13 1.7 1	-79/3A
Germany 1979	EC	2	0.75	0.13	0 14 21 28 35	 <0.08 <0.06	 <5.9 <4.8 <3.6	17 2.8	-79/4A
Germany 1979	EC	2	0.75	0.13	0 15 22 29	 <0.06 <0.06	 <3.3 <2.6	9.1 1.8	-79/5A

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					36	0.06	2.9		
Germany 1979	EC	2	0.75	0.13	0 18 25 32 39	 <0.05 <0.05	 2.8 2.7	5.1 1.9 1.3	-79/6A
Germany 1979	EC	2	0.75	0.13	0 21 28 35	 0.08	 0.9	14 1.1 1.1	-79/7A
Germany 1979	EC	2	0.75	0.13	0 21 28 35 42	 <0.05 0.05 <0.05	 1.2 2.1 1.8	5.2 1.2	-79/8A
Germany 1979	EC	2	0.75	0.13	0 21 28 35 42	 0.07 0.09 0.07	 4.4 4.2 4.3	14 3.9	-79/9A
Germany 1979	EC	2	0.75	0.13	0 21 28 35 42 49	 <0.05 <0.05 <0.05	 1.1 0.8 0.8	13 0.8 0.5	-79/10A
Germany 1979	EC	2	0.75	0.13	0 28 35 42 49	 <0.05 <0.05	 3.4 2.7	22 1.2 0.9	-79/18A
Germany 1979	EC	2	0.75	0.13	0 28 35 42	 <0.05	 1.2	20 0.6 0.6	-79/19A
Germany 1979	EC	2	0.75	0.13	0 28 35 42 49	 <0.05 <0.05	 1.2	26 0.6 0.5	-79/20A
Germany 1982	SC[3]	1	0.6	0.12	0 21 28 35 42 57 controls	 0.2(E) <0.05 <0.05 <0.05 <0.05	 1.1 1.2 1.1 1.2 <0.1	7.9 0.6	43805F-82/4A
Germany 1983	SC[3]	1	0.6	0.15	0 21 36	 0.7(E) 0.2	 2.3	32	-83/7A[4]
Germany 1983	SC[3]	1	0.6	0.15	0 21 35 42	 0.2 0.2	 1.9 2.4	39 3.8	-83/8A[4]

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					49	0.3	2.2		
Germany 1983	SC[3]	1	0.6	0.15	0 21 35 42 49	 1.5(E) 1(E) 0.2(E) 0.2	 2.2(stlk) 2.3(stlk) 3(stlk) 2.3	38	-83/9A[4]
Germany 1983	EC[5]	2	0.56	0.14	0 21 28 35 42	 0.14(E) 0.1 <0.05 <0.05	 0.5(stlk) 1 0.7 0.6	6.2	46400F-88/6A[6]
Netherlands 1981	SC[3]	1	0.75	0.18-0.25	61-62	<0.05(8)	≤0.1(3), 0.2, 0.4, 0.5, 0.6(2)		43803F-81/1E, /2E, /3E, /4E, /5E, /6E, /7E, /8E
Sweden 1980 2 trials	EC	1	0.56/ 0.75	0.02/ 0.03	95	<0.05(2)			42100F-80/22E, /23E
Sweden 1981 2 trials	EC	1	0.75	0.19	88, 90 controls	<0.05 --	0.06, 0.08 <0.05		82064/g, /h
Sweden 1980	EC	1	0.75		--	<0.05			80071
Winter wheat									
Denmark 1979	EC	1	0.75 1.1 0.75 1.1		99 99 91 91 controls	<0.05 <0.05 <0.05 <0.05 <0.05	0.05 <0.05 0.1 0.2 <0.05		79069/c 79069/d
Denmark 1980	EC	1	0.56 0.75 0.75		83 83 69		0.2 0.4 0.6		80092
Denmark 1980	EC	1	0.75		99	<0.05	0.2		80093
Denmark 1980	EC	1 2	0.56 0.75 0.75		85 85 43 controls	<0.05 <0.05 0.05 <0.05	0.4 0.5 1.6 --		80099
Denmark 1982	EC	1 2 2	0.38 0.38 0.75		55 36 36 controls			0.1 0.2 0.3 <0.05	82080
Denmark 1982	EC	2	0.38 0.75 0.75		55 36 36 controls			0.2 0.3 0.6 <0.05	82081
Denmark 1982	EC	1 2 2	0.38 0.38 0.75		104 85 85 controls	<0.05 <0.05 <0.05 <0.05	0.2 0.7 0.8 <0.05		82101
Denmark 1982	EC	1 2 2	0.38 0.38 0.75		96 77 77 controls	<0.05 <0.05 <0.05 <0.05	0.3 1 2.3 0.08		82102
Denmark 1982	SC[3]	1	0.6	0.15	66	<0.05	0.4		43805F-82/13E
Denmark 1983	SC[7]	1	0.75	0.19	32 61	 <0.05(E)	 0.4(stlk)	0.4	43102F-83/1A

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					95	<0.05	0.5		
Denmark 1983	SC[7]	1	0.75	0.19	31 60 96	 <0.05(E) <0.05	 0.2(stlk) 0.2	0.2	-83/2A
Denmark 1984	EC	2 2	0.56 0.56		70 73 controls	<0.05 <0.05 <0.05	1.6 1 0.3		85053 85054
Denmark 1984 2 trials	EC[8]	2	0.56	0.28	70, 73 controls	<0.05(2) <0.05	1.7, 0.09		85075, 85076
Denmark 1990	EC[8]	2	0.38	0.19	0 18 32 43 57 controls	 <0.02 <0.02	 0.04 <0.02	1.8 0.1 0.05 0.03 <0.02-0.03	2142/91[4]
Denmark 1990	EC[8]	2	0.75	0.38	0 18 32 43 57 controls	 <0.02 <0.02	 0.05 <0.02	7 0.3 0.1 0.08 <0.02-0.03	2143/91[4]
Denmark 1990	EC[8]	2	0.38	0.19	0 20 31 42 63 controls	 <0.02 <0.02	 0.08 <0.02	3.3 0.3 0.2 0.3 <0.02-0.07	2144/91[4]
France 1978 3 trials	EC	1	1.1	0.19	45 54 79	<0.05 <0.05 <0.05	0.2 0.1 0.1		42100F-78/13E, /14E, /15E
France 1979 3 trials	EC	1	0.75	0.13	42 48 49	<0.05 <0.05 <0.05	1.9 0.6 1.5		-79/8E, /9E, /10E
France 1979	EC	2	0.75	0.15	49 controls	<0.05 <0.05	0.8 <0.05		79033
France 1979	EC	1	0.75 1.1		59 59 controls	<0.05 <0.05 <0.05	0.1 0.1 <0.05		79040
France 1979	EC	1 2	0.75 0.75		70 71	<0.05 <0.05	0.06 0.1		79047 79046
France 1979	EC	2	0.75 1.1		30 30 controls	<0.05 0.06 <0.05	0.6 0.8 0.06		79056
Germany 1981	EC	**3**	0.75	0.13	0 21 28 35 42 52	 0.5(E) 0.5(E) <0.05 <0.05	 2.3 2.9 2.3 2.3	18 1.2	42100F-81/3A
Germany 1981	EC	**3**	0.75	0.13	0 21 28			21 2.1 2	-81/4A

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					35 42 62	1.2(E) 0.08 0.07	4.5 3.3 1.4		
Germany 1981	EC	**3**	0.75	0.13	0 21 28 35 42 controls	 0.4(E) <0.05 <0.05 <0.05	 2.5 2.7 2 <0.1	8.1 1.6 <0.1	-81/9A
Germany 1981	EC	**3**	0.75	0.13	0 21 28 35 42 62 controls	 0.5(E) <0.05 <0.05 <0.05	 2 2.3 0.9 <0.1	14 1.2 1.2 <0.1	-81/8A
Germany 1987	EC[9]	2	0.56	0.14	0 16 28 37 43 59 controls	3.4(E) 0.3(E) 0.3(E) 0.4 0.4 <0.05 <0.05	 0.8 0.5 0.7 <0.05		87072
Germany 1988	EC[5]	2	0.56	0.14	0 21 28 35 42	 0.1(E) 0.1(E) <0.05 <0.05	 0.4 0.2 <0.05 0.8 yes	1.4	46400F-88/3A
Germany 1988	EC[5]	2	0.56	0.19	0 21 28 35 42	 0.1(E) <0.05 <0.05 <0.05	 0.2(stlk) 0.7 0.3 0.2	7	-88/4A
Germany 1982	SC[3]	1	0.6	0.1	0 21 28 35 42 controls	 0.5(E) 0.7(E) <0.05 <0.05 <0.05	 1.8 1.6 1.8 1.5 <0.1	13 <0.1	43805F-82/1A
Germany 1982	SC[3]	1	0.6	0.15	0 21 28 35 41 54 controls	 0.4(E) 0.07(E) 0.06 <0.05	 1.7 2 1.4 <0.1	6.4 1.1 1.1 <0.1	-82/2A
Germany 1982	SC[3]	1	0.6	0.15	0 21 28 35 43 50 controls	 <0.05(E) <0.05 <0.05	 1.1(stlk) 0.6 <0.1	8 0.7 0.4 0.6 <0.1	-82/3A
Germany 1983	SC[3]	1	0.6	0.15	21 35 42	 0.9(E) 0.2	 1.6(stlk) 2.4	6.2	-83/3A

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					49 controls	0.1 <0.05	2.1 <0.1	<0.1	
Germany 1983	SC[3]	1	0.6	0.15	0 21 35 42 49	 0.4(E) 0.4 0.3 0.2	 0.6(stlk) 0.7 0.7 2.3 yes	17	-83/4A[4]
Germany 1983	SC[3]	1	0.6	0.15	0 21 35 42 49	 1.2(E) 0.4 0.4	 1.2(stlk) 1.2 1.1	15 6.5	-83/5A[4]
Germany 1983	SC[3]	1	0.6	0.15	0 21 36 43	 0.4(E) 0.3	 0.6(stlk) 0.8	31 3.9	-83/6A[4]
Netherlands 1979 3 trials	EC	1	0.75	0.25	65	<0.05(3)	0.4, 0.4, 0.6		42100F-79/22E, 23E, 24E
Netherlands 1979 4 trials	EC	1	0.75	0.2	72	<0.05(4)	2.4, 2.3, 2.5, 2		-79/25E, 26E, 27E, 28E
Netherlands 1979 4 trials	EC	2	0.75	0.25	71	<0.05(4)	0.3, 0.4(3)		-79/13E, 16E, 18E, 19E
Netherlands 1979 4 trials	EC	1	1.1	0.38	71	<0.05(4)	0.2, 0.3(2), 0.4		-79/14E, 15E, 17E, 20E
Netherlands 1979	EC	1 1 2	0.75-1.5 0.75, 1.1 0.75		101 87 87 controls	<0.05(3) <0.05(2) <0.05 <0.05	0.08, 0.1(2) 0.09, 0.1 0.2 <0.05		79078
Netherlands 1979	EC	1 2	0.75-1.5 0.75		92 71 controls	<0.05(3) <0.05 <0.05	<0.05, 0.08, 0.1 0.3 <0.05		79079
Netherlands 1979	EC	1	0.56, 0.75		76 controls	<0.05(2) <0.05	0.2(2)		79080
Netherlands 1979	EC	1	0.56 0.75		56 56 controls	<0.05 <0.05 <0.05	0.2 0.1 <0.05		79083
Netherlands 1979	EC	1 2	0.56 0.75		77 59 controls	<0.05 <0.05 <0.05	<0.05 0.07 <0.05		79084
Netherlands 1980	EC	2	0.75 0.94		67 67 controls	<0.05 <0.05 <0.05	0.8 1.2 <0.05		80056
Netherlands	EC	2	0.75		63 controls	<0.05 <0.05	0.8 <0.05		80075
Netherlands 1980 7 trials	EC	1	0.75		10 20 31 38 45	0.07 0.1 <0.05 <0.05 <0.05	1.3 2 0.4 1.2 1.2		80076

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
					53 61 controls	<0.05 <0.05 <0.05	0.9 0.5 <0.05		
Netherlands 1980 6 trials	EC	1-2 1-2 1	0.75 0.75 0.75		51 74 251 controls	<0.05(3) <0.05(2) <0.05 <0.05	0.6, 0.7, 2.7(1 appl.) 0.2, 0.3 0.06 <0.05		80077
Netherlands 1980 2 trials	EC	1	0.75		62 76 controls	<0.05 <0.05 <0.05	0.4 0.3 <0.05		80080
Sweden 1980 3 trials	EC	1	0.75		--	<0.05(3)			80067, -68, -70,
Sweden 1981 3 trials	EC	1	0.75	0.19	96-101 controls	<0.05(3) --	0.09, 0.2(2) <0.05		82064/d, /e, /f
Sweden 1981 2 trials	EC	1	0.75	0.19	88, 90 controls	<0.05	0.08, 0.06		82064/g, /h
Sweden 1984	EC[8]	2	0.56	0.28	73 controls	<0.05(2) <0.05	0.9 --		85076
Sweden 1982 5 trials	SC[3]	1	0.6	0.13	57-80	<0.05(5)			43805F- 82/7E, /8E, /9E, /10E, /11E
Sweden 1983 3 trials	SC[3]	1	0.6		58-67	0.3, 0.3, 0.4			-83/9E, /10E, /11E
Sweden 1981 2 trials	SC[3]	1	0.56		70	<0.05(2)			43800F-81/1E, /2E
Sweden 1984 4 trials	SC[7]	1	0.75	0.19	98-126	<0.05 (4)			43102F-84/1E, /2E, /3E, /4E
Switzerland 1979	EC	2	0.75	0.15	0 14 27 41 55 controls	 <0.05 <0.05	 <0.05 <0.05	6.2 0.5 0.2 0.2 0.2 0.2	79015
Switzerland 1981	EC	1	0.56		1 9 21 42 56 controls	 <0.05 <0.05	 0.5 <0.05	1.9 0.7 0.4 0.2	81044
Switzerland 1981	EC	2	0.75		56 controls	<0.05 <0.05	1 <0.05		81074
Switzerland 1981	EC	2 1	0.75 0.56		59 59 controls	<0.05 <0.05 <0.05	0.5 0.2 <0.05		81078 81079
UK 1978 4 trials	EC	1	1.1	0.5	69 78	<0.05(2) 0.05(2)	<0.05, 0.08 0.08, 0.2		42100F- 78/4E, /5E,/6E, 7E
UK 1979	EC	1	0.75	0.3	0 7			6.7 1.3	42100F- 79/14A

Country, year, (variety)	Application				PHI, days	Fenpropimorph, mg/kg[1]			Ciba, 1994 Report No.
	Form.	No.	kg, ai/ha	kg, ai/hl		Grain (E=ear)	Straw	Whole plant	
			(1.5X)		14 21			1.1 0.6	
UK 1979	EC	1	1.5	0.75	28 77	0.07 <0.05	6 7.7		-79/15A
UK 1979	EC	1	1.1	0.5	27 62	1.1(E) <0.05	0.3 1.4		-79/16A
UK 1979	EC	1	1.1	0.5	93	<0.05	1.8		-79/12E
UK 1979 2 trials	EC	1	0.75	0.38	34 84	<0.05 <0.05	3.2 1.7		-79/31E -79/44E
UK 1979 2 trials	EC	2	0.75	0.38	34-36 41	<0.05 <0.05	3.8 3.3		-79/46E -79/47E
UK 1979 2 trials	EC	1	1.1	0.56	34 91	<0.05 <0.05	3.3 1.8		-79/30E -79/48E
UK 1979 2 trials	EC	2	1.1	0.56	34 41	<0.05 <0.05	4.1 4.9		-79/45E -79/49E
UK 1979	EC	1 2 2	1.1 1.1 1.1 0.75	0.53 0.36	84 34 34 34 controls	<0.05(2) <0.05(2) <0.05,0.05 <0.05(2) <0.05	0.3, 0.2 0.4, 0.5 0.5, 0.7 0.5, 0.4 0.1		79065
UK 1979	EC	1 1 2 2	1.1 1.1 1.1 0.75	0.53 0.36	88 41 88/41 88/41	0.05(2) <0.05(2) <0.05(2) <0.05	0.05,0.08 0.2, 0.1 0.2(2) 0.2(2)		79066
Summer wheat									
Germany 1987	EC[9]	2	0.56	0.14	0 14 28 36 controls	3.1(E) 0.3(E) 0.2(E) <0.05 0.2(E) <0.05	 0.5 <0.05		87069
Netherlands 1980 2 trials	EC	1	0.56 0.75		70 70 controls	<0.05 <0.05 <0.05	0.2 0.3 <0.05		80078
Sweden 1980	EC	1	0.75 2.3		36 36 controls	<0.05 <0.05 <0.05	1 4 4[10]		80058

[1] Numbers in parentheses = no. of samples with that residue
[2] 300 g fenpropimorph + 500 g captafol/kg product
[3] 200 g fenpropimorph + 330 g chlorothalonil/1 product
[4] Although storage was at -20°C, sampling to analysis interval was excessive (3-4 yr.)
[5] 563 g fenpropimorph + 187 g tridemorph/1 product
[6] Summary data. Original reports were not in submission
[7] 375 g fenpropimorph + 175 g carbendazim/1 product
[8] 375 g fenpropimorph + 200 g prochloraz/1 product
[9] 281 g fenpropimorph, + 200 g prochloraz/1 product
[10] Control reported as 4 mg/kg. Mislabelling suspected

Beans. Data were available on fresh ripe bean seeds from 6 trials and on whole bean plants (including seeds and pods) from 3 trials in the UK. The results are shown in Table 22.

Table 22. Residues of fenpropimorph in beans resulting from supervised trials in the UK in 1983. All applications 0.75 kg ai/ha. All EC. All according to GAP.

Commodity (Cultivar)	Application		PHI, days	Fenpropimorph, mg/kg		Ciba, 1884, Report No.
	No.	kg ai/hl		Whole plant (incl. pods and seeds)	Seed (fresh ripe)	
Beans (Throws MS)	1 1 2	0.3	131 145 131	0.06 0.09 0.06		42100F-83/10E-83/8E-83/9E
Beans (Throws MS)	1	0.3	49		<0.05	-83/22E
Field beans	1	--	38		<0.1	-83/6E
Beans (Throws MS)	2	0.3	35		0.07	-83/23E
Field beans	2	0.22	29		<0.1	-83/3E
Field beans	2	0.22	26		<0.1	-83/4E
Field beans	2	0.3	72		<0.1	-83/5E

Leeks. Eight trials were conducted in the UK in 1982-3. Residues in whole plants are shown in Table 23. All trials were according to GAP.

Table 23. Residues of fenpropimorph in leeks (whole plants) resulting from supervised field trials in the UK. All applications were EC, 0.75 kg ai/ha, and according to GAP.

Year	Application		PHI, days	Residues, mg/kg	Report no.
	No.	kg ai/hl			
1983	3	0.15	23 35	0.2 0.2	42100F- 83/1A
1983	5	0.17	3 26	0.1 0.1	-83/2A
1982	4	0.21	21 38	0.3 0.2	-83/3A
1983	4	0.22	21	0.2	-83/11E
1983	4	0.22	21	0.4	-83/12E
1982	5	0.3	20	0.3	-82/7E
1983	5	0.19	29	<0.05	-83/7E
1983	3	0.13	124	<0.1	-82/8E

Sugar beet. Data from supervised trials in six countries were available in 29 reports. Application rates were within the range of reported Western European GAP, for which the shortest PHI is 7 days. The results are shown in Table 24.

Table 24. Residues of fenpropimorph in sugar beet resulting from supervised field trials.

Country, year	Application (kg ai/ha or /hl for mixed formulations refers only to fenpropimorph)				PHI, days	Fenpropimorph, mg/kg		Ciba, 1994 Report no.
	Form.	No.	kg ai/ha	kg ai/hl		Roots	Leaves	
Belgium 1985	EC	1	0.75	0.13	72 46 62 control	<0.02 <0.02 <0.02 <0.02	0.06 0.07 0.03 <0.02	86/10160 (= 86/200) 86/10161 86/10162
France 1983	EC	1 2 1	0.75	0.16	72 68 82	<0.05 <0.05 <0.05	0.2 0.3 0.09	42100F-83/13E- 83/14E-83/15E
France 1983	SC[1]	1 1 1 2	0.75	0.06	77 72 82 68	<0.05 <0.05 <0.05 <0.05	0.2 0.1 0.1 0.14	43102F-83/1E -83/2E -83/4E -83/3E
France 1982 1983 1982 1983 1983 1982 1982 1982	WP[2]	1 1 2 2 2 2 2 2	0.38	0.08	49 70 25 34 42 49 75 76 controls	<0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05	0.06 <0.05 0.1 0.07 0.08 <0.05 0.09 0.07 <0.05	82112 83105 82113 83106 83107 82114 82117 82118
Greece 1984	EC	3	1.1	--	0	--	2.6	84/10156

Country, year	Application (kg ai/ha or /hl for mixed formulations refers only to fenpropimorph)				PHI, days	Fenpropimorph, mg/kg		Ciba, 1994 Report no.
	Form.	No.	kg ai/ha	kg ai/hl		Roots	Leaves	
					3 6 9 12 15 18	-- -- -- -- -- --	1 0.6 0.4 0.3 0.3 0.2	
Italy 1989	EC	2	0.56	0.11	3 5 16 31 controls	<0.05 <0.05 <0.05 <0.05 <0.05	0.8 1.6[3] 0.2 0.06 <0.05	49100F-89/3E -89/4E -89/1A -89/1A
Italy 1989	EC	3	0.56	0.14	1 7 13 32	<0.05 <0.05 <0.05 <0.05	0.2 0.9 0.3 0.14	452100F89/2A
Italy 1988	EC	3	0.56	0.11	2 8 15 30	<0.05 <0.05 <0.05 <0.05	0.5 0.8 0.3 1	42100F88/8A
Italy 1987	EC	3	0.75	0.19	20	<0.05	<0.05	42100F87/12E
Sweden 1985	EC	3	0.75	0.3	65	<0.05	0.2	42100F85/7E
Switzerland 1988	EC[4]	2	0.56	0.07	96 113	<0.05	0.3 <0.05	88150
Switzerland 1988	EC[4]	2	0.56	0.07	76 94	<0.05	0.3 0.1	88151
Switzerland 1988	EC[4]	1	0.75	0.19	51	<0.05	1	88152

[1] 375 g fenpropimorph + 125 g carbendazim/1 product
[2] 188 g fenpropimorph + 50 g carbendazim + 400 g mancozeb/kg product
[3] An anomalous 1.6 mg/kg is the reported value. No explanation. Ripe leaf
[4] 375 g fenpropimorph + 225 g prochloraz/1 product

In animals

Of the crops for which maximum residue levels have been estimated by the Meeting, those which may be fed to animals include the grains, straws, forage and fodders of cereals, and sugar beet tops. No information was available on residues in sugar beet molasses or pulp.

Many assumptions might be made for estimating residue levels in animal products. A theoretical, if perhaps unlikely, worse-case beef cattle diet might be 65% grain, 25% cereal forage and 10% dry cereal straw and fodder. That of a dairy cow might be 40% grain, 50% cereal forage and 10% dry cereal straw and fodder. Poultry might be fed cereal grain up to 70% of the diet. Assuming that fenpropimorph residues might occur up to 0.5 mg/kg in cereal grain, up to 2 mg/kg in fresh cereal forage, up to 5 mg/kg in dry cereal straw and fodder, and up to 1 mg/kg in sugar beet leaves, the maximum theoretical dietary intakes of fenpropimorph would be 1.3 ppm for beef cattle, 1.7 ppm for dairy cattle and 0.35 ppm for poultry if sugar beet leaves, which contribute least to the theoretical intake, are excluded.

No conventional feeding trials were reported to the Meeting. The goat metabolism studies described earlier were at 0.6 ppm (Hawkins *et al.*, 1980a, morpholine label), 1421 ppm (morpholine label) and 2335 ppm (phenyl label) (Ritter, 1989a) in the diet. The feeding levels for hens were 51.5

ppm (phenyl label) and 39.3 ppm (morpholine label) (Ritter, 1989b). Only the 0.6 ppm feeding level in goats and the feeding levels in the hens are even remotely close to expected dietary intakes. The total residues, expressed as fenpropimorph, that might occur in tissues, milk and eggs under worse-case assumptions of 1.7 ppm in the diet of cattle and 0.35 ppm in that of poultry are presented in Table 25. Calculations based on the higher-level goat metabolism studies yield somewhat lower estimates than those shown in Table 25.

Table 25. Theoretical estimates of total residues, expressed as fenpropimorph, in cattle and poultry calculated from metabolism studies on goas and hens.

Sample	Residues, mg/kg fenpropimorph equivalents					
	Found in goats receiving 0.6 ppm	Calculated in cattle[1]	Found in hens receiving 41 ppm	Calculated in poultry[2]	Found in hens receiving 55 ppm	Calculated in poultry[3]
Muscle	0.004	0.01	0.4	0.003	0.34	0.002
Fat	0.012	0.03	1.4	0.01	1.1	0.007
Liver	0.103	0.3	2.8	0.02	3.9	0.025
Kidneys	0.029	0.08	2.8	0.02	2.4	0.05
Milk	0.008	0.02				
Eggs			0.5	0.004	1.7	0.01

[1] Assuming 1.7 ppm intake. Factor = 1.7/0.6 = 2.8
[2] Assuming 0.35 ppm intake. Factor = 0.0085
[3] Assuming 0.35 ppm intake. Factor = 0.006

The relevance of these calculations to the estimation of maximum residue levels for animal products is discussed in the appraisal.

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

Citrus fruit were dipped in a 1500 mg/l aqueous solution of fenpropimorph and analysed for residues after 2 days at room temperature and 30 days at 5°C (Lafuente *et al.*, 1986). The results are shown in Table 26.

Table 25. Fenpropimorph residues (mg/kg) in citrus stored for 2 days and 30 days after dip treatment at 1500 mg/l (Lafuente *et al.*, 1986).

Sample	Washington navel oranges		Hernandina clementines	
	2 days[1]	30 days[2]	2 days[1]	30 days[2]
Whole fruit	1.9	0.73	1.0	0.79
Peel	5.2	2.8	4.6	4.1
Albedo	0.46	0.41	1.2	1.1
Pulp	0.04	0.05	0.05	0.07

[1] Room temperature
[2] 5°C

In processing

Four summary reports were available on the processing and baking of wheat.The results are shown in Table 27.

Table 27. Residues in processed fractions of wheat field-treated with fenpropimorph at 0.75 kg ai/ha.

Reference	Sample	Residue, mg/kg, after interval (days)		
		35	46	169-189
BASF 1979a	grain rolls	0.08		 <0.05
BASF 1979b	grain rolls	0.05		 <0.05
BASF 1979c	grain rolls	0.06		 <0.05
BASF 1985	grain grain after cleaning wholemeal wholemeal bread bran semolina bran "Nachmehl" white flour white bread		<0.05[1]	 0.07 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05 <0.05

[1] 59% recovery

Residues in the edible portion of food commodities

Cereal grains are the only edible food commodities in which the estimated maximum residue levels are above the LOD. The data indicate that median residues in grain are likely to be <0.05 mg/kg and maximum residues unlikely to exceed 0.5 mg/kg. As noted above, summary reports suggest that residues in processed grain fractions are likely to be lower than in grain, and residues would probably not be detectable (<0.05 mg/kg) in bread on the basis of the median residues expected in grain. These conclusions need to be confirmed.

Fenpropimorph residues in citrus pulp from post-harvest dip treatments are likely to be less than 10% of those in the whole fruit (Table 26).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided.

NATIONAL MAXIMUM RESIDUE LIMITS

Information on national MRLs was provided for 11 countries in which fenpropimorph is registered.

National maximum residue limits for fenpropimorph.[1]

Commodity	Country	MRL (mg/kg)

Commodity	Country	MRL (mg/kg)
Cereal grains	Austria	0.5
	Belgium	0.2
	France	0.1
	Germany	0.5
	Hungary	0.05
	Italy (barley, oats, rye, wheat)	0.5
	Luxembourg	0.2
	Netherlands	0.05
	New Zealand	0.5
	Spain	0.2
	Switzerland	0.1
	Taiwan	0.1
Cereal straw	Hungary	0.5
	Spain	1
Leeks	Belgium	0.5
	Netherlands (December 1993)	0.5
Milk	Netherlands (December 1993)	0.05
Meat	Netherlands (December 1993)	0.05
Other food and feedstuffs of plant origin		
	Austria	0.1
	Belgium	0.05
	Germany	0.1
	Netherlands	0.05
	Spain	0.05

[1] All MRLs are for fenpropimorph *per se*, including those for milk and meat in The Netherlands

APPRAISAL

Fenpropimorph is a fungicidal pesticide whose major use is for the control of diseases in cereals. It is formulated into more than 49 products, mostly in mixtures with other fungicides, although the EC formulation is reported to be the most commonly used. Typically 1-3 field applications are made at rates of 0.3 to 0.75 kg ai/ha. Fenpropimorph was reviewed for the first time at the 1994 JMPR which considered toxicological aspects. Owing to the late receipt of residue data the FAO Panel review was postponed until 1995.

The fate of residues has been studied in animals, plants, soil, water and soil/water systems. The metabolism in plants is similar to that in animals to the extent that oxidation is the first stage of metabolism, followed by degradation of the morpholine ring. There are differences, especially in that generally fenpropimorph is the main residue in plants but is not found in animals (fenpropimorph reported in hen kidneys is an exception).

The metabolites referred to by codes are identified below.

BF 421-1	4-{3-[4-(2-hydroxy-1,1-dimethyl)ethylphenyl]-2-methylpropyl}-*cis*-2,6-dimethylmorpholine
BF 421-2	2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionic acid
BF 421-2-Me	methyl 2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)propyl]phenyl}propionate
BF 421-2 conjugate	2-methyl-2-{4-[2-methyl-3-(*cis*-2,6-dimethylmorpholin-4-yl)-propyl]phenyl}propionic acid conjugate

BF 421-3	2-methyl-2-{4-[2-methyl-3-(*cis*-2-hydroxymethyl-6-methylmorpholin-4-yl]propyl)phenyl}propionic acid
BF 421-4	2-methyl-2-{4-[2-methyl-3-(2-hydroxypropyl)aminopropyl]-phenyl}propionic acid
BF 421-7	[3-(4-*tert*-butylphenyl)-2-methylpropyl](2-hydroxypropyl)amine
BF 421-10	*cis*-2,6-dimethylmorpholine
BF 421-13	4-[3-(4-*tert*-butylphenyl)-2-methyl-1-oxopropyl]-*cis*-2,6-dimethylmorpholine
BF 421-15	4-[3-(4-*tert*-butylphenyl)-2-methylpropyl]-*cis*-2,6-dimethylmorpholine-3-one
BF 421-16	2-methyl-2-[4-(carboxyphenyl)]propan-1-ol
BF 421-17	2-methyl-2-[4-(2-carboxypropyl)phenyl)]propionic acid

The Meeting noted that the animal metabolites (and/or their conjugates) BF 421-3, BF 421-4, BF 421-16 and BF 421-17 had not been reported in plants. The plant metabolites BF 421-2-Me, BF 421-7, BF 421-10, BF 421-13 and BF 421-15 have not been reported in animals. Residues of most of these would be expected to be less than 1/4 of those of the parent compound, although BF 421-7 has been reported in one study of wheat metabolism to be at a similar level to the parent compound in wheat straw under some conditions. In any future animal metabolism studies it may be prudent to analyse for these plant metabolites.

Studies on rats, goats and poultry show rapid absorption from the gastrointestinal tract and rapid elimination of residues in the faeces, urine or excreta, slightly less in the urine than the faeces. High bile residues were consistent with a high rate of faecal elimination.

The three test animals showed similar but not identical metabolism, consisting mainly in progressive oxidation of methyl groups of both the *tert*-butyl group and the morpholine ring. Further metabolism of the morpholine ring was demonstrated by the expiration of significant amounts of $^{14}CO_2$ by the rat. The expiration of $^{14}CO_2$ was not measured in goats or hens.

In animals, residues of the parent compound were detected only in hen kidneys. The highest residues of identified metabolites were in the liver and kidneys. The main metabolites were BF 421-1, detected in goat fat and faeces and hen plasma, BF 421-2 detected in several goat tissues and milk and hen kidneys and liver, and BF 421-3 detected in goat and hen kidneys and goat fat.

No conjugates were detected in hens, whereas conjugates of BF 421-2 were found in goat liver and a conjugate of BF 421-3 was found only in rat urine, faeces and bile. Metabolites BF 421-16 and BF 421-17 were detected only in rat urine, kidneys and faeces.

Although the faeces and urine were by far the predominant routes of elimination of residues, approximately 50% of the material administered to goats in one study was not accounted for by analyses of the urine, faeces, milk, bile, cage washes, and tissues or organs, and was assumed to remain in the gastrointestinal tract. This was not documented nor was radioactivity measured in expired CO_2, which had been shown to be a significant route of elimination in rats. Elimination in the faeces and urine combined was reported to be about 84% in a separate study in which animals were killed 24 hours after the last dose as compared with 5 hours in the first study.

In studies of cereal metabolism fenpropimorph with the benzylic carbon labelled was applied to leaf surfaces. Over 60% of the residue on the day of application was on the leaf surface and was mainly unchanged fenpropimorph. After three weeks about 30% of the applied radioactivity was absorbed into the leaf and only about 7% of that was unchanged fenpropimorph. Low levels of radioactivity were translocated to untreated plant parts. With the ring-labelled compound (either ring) most of the radioactivity was extractable and fenpropimorph was generally by far the main residue, although BF 421-7 was sometimes of the same order in straw, depending on the conditions. Other metabolites identified in cereal plants included BF 421-1, BF 421-2, BF 421-2-Me, BF 421-10, BF

421-13 and BF 421-15. The underlined compounds were not reported in studies of animal metabolism.

The radioactivity in cereal grains was too low for identification and was mainly associated with the starch fractions, although it did not appear to be incorporated into the glucose units. Less was associated with protein and polysaccharide fractions.

Rotational crop plantings in soil containing 0.42 mg/kg [^{14}C]fenpropimorph resulted in residues in the mature crop of ≤0.01 mg/kg fenpropimorph equivalents in spinach and sugar beet tops, <0.02 mg/kg in green wheat plants and 0.004 mg/kg in mature sugar beets. Since metabolism studies showed relatively rapid degradation of fenpropimorph, the rotational crop data suggest that, at least in sandy loam soil, only trace residues would be expected in rotational crops after the previous crops had been sprayed with fenpropimorph.

Under neutral conditions fenpropimorph is largely stable in water. Degradation in soil proceeds by oxidation and opening of the morpholine ring to give BF 421-2, BF 421-7, BF 421-8 and BF 421-10. In addition, BF 421-13 and BF 421-15 can result from the photolysis of soil residues. The half-life of fenpropimorph in soil varies according to the conditions, ranging from 10 to 90 days. In aerobic water/sediment systems degradation is similar, except that the morpholine ring is not opened.

Analytical methods are available for the determination of fenpropimorph in plant materials, soil and water. For plants the emphasis in method development has been on cereals (grain, plant, forage and straw) and citrus. Most methods rely on extraction with methanol, chloroform, methylene chloride or other solvents and concentration, with or without clean-up by cation exchange, alumina chromatography or liquid/liquid partition. Determination is generally by GLC with an NPD or occasionally HPLC with UV detection or GC-MS, depending on the method and the matrix being analysed. A limit of determination of 0.05-0.1 mg/kg should be achievable in most cases and perhaps lower, especially for water, soil and grain. However, for some methods sufficient information was not available for an independent estimate of the limit of determination.

Methods for fenpropimorph acid (BF 421-2) in soil depend on methylation with diazomethane before determination by GLC with an NPD or by GC-MS.

The stability of fenpropimorph in stored analytical samples of wheat grain, green plants and straw and of fenpropimorph and its acid in soil was investigated over a 2-year period. The maximum losses of the parent compound or its acid were about 25%, but generally less than 10%.

Because residues in plants are generally mainly the parent compound the Meeting concluded that for regulatory purposes the residue in plants should be defined as fenpropimorph. For risk assessment purposes, the data suggest 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 more likely less than twice that level. Consideration of a definition of the residue in animal products must await further information. The Meeting was informed by the manufacturer that national definitions of the residue in foods and feeds of plant origin include only fenpropimorph. This is also the definition for residues in meat and milk in The Netherlands.

Supervised residue trials gave the following results.

Beans. Residues in fresh ripe bean seeds in 6 trials in 1983 in the UK at GAP rates were <0.05, <0.1 or 0.07 mg/kg after 26-72 days compared to the 28-day UK PHI. Residues in 3 UK trials, also according to GAP, were 0.06(2) and 0.09 mg/kg in whole plants. The results suggest that residues are unlikely to exceed 0.1 mg/kg in fresh shelled beans, but because the data were relatively old and limited and the residue reports did not include information on method(s) of analysis, sample chromatograms, control values, or analytical recoveries, the Meeting concluded that the information

was insufficient to support a limit.

Carrots. The Meeting did not use summary data submitted from Norway in the absence of detailed reports, acknowledged to be unavailable.

Cereals. Data from many supervised trials with a wide geographical distribution (mainly Western Europe) were available. A significant number of the reports were not sufficiently documented for full confidence in the validity of the data, but because over half of the reports were considered reasonably well documented and because of the similarity and mutual support of the results among the cereals, the Meeting concluded that limits could reasonably be recommended, even when discounting the less well documented studies. In most cases grain residues were less than 0.05 mg/kg.

Most of the trials were on barley and wheat. Although the results were minimal for oats and somewhat scanty for rye, the Meeting considered the data on cereal grains to be mutually supportive.

Barley. Over 100 supervised trials were conducted in 9 Western European countries and New Zealand, covering the range of reported GAP including 1-3 applications, usually of EC formulations, at rates ranging from 0.38 to 0.75 kg ai/ha and PHIs ≥30 days. Data were also available for exaggerated rates and shorter PHIs. Residues in barley grain judged by the Meeting to be from treatments according to GAP, expressed as mg/kg with the number of results in parentheses were/ ≤0.05 (62), <0.08 (2), 0.06 (3), 0.07 (4), 0.08 (3), 0.09 (4), 0.1 (12), 0.2 (8), 0.3 (2), 0.4 (2) and 0.5 (1), with a median of <0.05 mg/kg. The residues of 0.3 mg/kg (from the same trial), 0.5 mg/kg and one of 0.4 mg/kg were from German trials according to German GAP, but with 3 applications instead of the two allowed. GAP in the UK allows three applications if the last two are after January as they were in these trials. The distribution in barley straw was ≤0.1 (29), 0.2-0.5 (23), 0.6-1 (19), 1.1-1.5 (13), 1.8 (4), 1.9 (1), 2.2 (1) and 4.2-4.8 (2). The last two residues were from the same German trial as the residues of 0.3 mg/kg in the grain. In whole barley plants residues from applications according to GAP at the days PHI in parentheses were 2.4-31 mg/kg (0), 7.3 mg/kg (7-9), 0.2-2.6 (14-18), 0.08-2 (20-25), 0.09-1.8 (26-30), 0.05-0.2 (30-40) and 0.04-0.07 mg/kg (40-50).

Although there was an adequate number of results, there were deficiencies in the detail provided for a significant number of the trials. For example, the sample handling and storage conditions and analytical recovery values were not provided, nor were analytical methods identified for about a third of the studies. No sample chromatograms were provided for any of the field studies, although representative chromatograms from grain and straw analyses were provided in separate validations of one of the methods used (Method 840-MD-02).

By putting greater weight on the better documented studies and noting that data among the cereals were similar and mutually supportive, the Meeting estimated a maximum residue level of 0.5 mg/kg for barley grain. No data on moisture content were available to estimate a maximum level in fodder on a dry weight basis, but with maximum expected residues of 2 mg/kg in fresh barley forage from GAP treatments, and assuming 30% dry matter, a theoretical level of 7 mg/kg could be estimated for dry fodder. Observing that median residues in fresh forage after the shortest GAP PHI would be <0.5 mg/kg, and noting maximum residues in barley straw of 4.8 mg/kg, the Meeting estimated a maximum residue level of 5 mg/kg for dry barley straw and fodder.

Wheat. Over 150 supervised trials were conducted in 10 Western European countries and in New Zealand. Some of the German trials were with higher application rates than reported German GAP, but as they were according to the GAP of neighbouring countries the Meeting considered that they should not be disregarded. The distribution of residues, with the number of results within reported GAP in parentheses, were for grain <0.05 (203), 0.05-0.09 (18) and 0.1-0.4 (20), with a median of <0.05 mg/kg, and for straw <0.05 (9), 0.05-0.09 (31), 0.1-0.4 (59), 0.5-0.9 (39), 1-2 (32), 2.1-2.9 (26), 3-4 (9), 4.1-5 (7) and 5.9 mg/kg, with a median of 0.7 mg/kg. Residues in whole plants were 0.08-39

mg/kg at day 0, decreasing to about 0.05-1 mg/kg at 30-60 days.

As in the case of barley some of the studies were not well documented, especially with respect to sample handling and storage conditions and the identification or provision of the analytical methods used. In approximately 6 cases the interval from sampling to analysis was ≥2 years and in four trials the plot size was only 5 m^2. No representative chromatograms were provided with the supervised trials data although, as with barley, they were provided with some method validations. The Meeting considered the documentation for approximately 7% of the 150 trials to be unacceptable. Approximately 50% were reasonably well documented and another 40% fairly well documented.

As with barley, the Meeting gave greater weight to the better documented studies, took into account the similarities among the different cereals, and estimated a maximum residue level of 0.5 mg/kg for wheat grain. Noting that only one residue (of 5.9 mg/kg) in over 250 barley and wheat straw samples exceeded 5 mg/kg, the Meeting concluded that it was unlikely that residues in straw would exceed 5 mg/kg.

Again, no moisture contents were available to estimate fodder residues on a dry weight basis. Assuming 25% moisture in the whole plants, and estimating a maximum residue of 2 mg/kg in fresh wheat fodder (whole plants), a theoretical maximum level of 8 mg/kg could be estimated for the fodder on a dry weight basis. Observing that, as in the case of barley,the median residue in fresh fodder after the minimum 30-day GAP PHI is likely to be less than 0.5 mg/kg compared with the estimated maximum of 2 mg/kg, the Meeting estimated a maximum residue level of 5 mg/kg for wheat straw and fodder, dry.

Oats. Data were available from three supervised trials in the UK in 1980, all within reported UK GAP for the EC formulation (2 x 0.75 kg ai/ha; 30-day PHI). Residues in grain were <0.05 (2) and 0.4 mg/kg after 35 days and <0.05 mg/kg after 81-83 days, in straw 1.2 and 0.8 mg/kg after 83 and 35 days respectively, and in green plants up to 1.1 and 0.5 mg/kg after 38 and 49 days respectively. The studies were reasonably well documented, except that the analytical method used was not identified. Taking into account the mutual support of the barley and wheat data, the Meeting estimated maximum residue levels of a 0.5 mg/kg for oat grain and 5 mg/kg for oat straw and fodder, dry.

Rye. Data were available for about 12 supervised trials conducted in 1980-84 in Germany, the UK and Sweden. Swedish trials with EC formulations were according to GAP reported for the UK and Germany, which allows up to two 0.75 kg ai/ha applications of the EC with a 35-day PHI.

Four of the Swedish trials with an SC formulation were within reported UK GAP for SC but two trials giving residues of 0.3 and 0.4 mg/kg after 82 days were from two applications at 0.75 kg ai/ha whereas UK GAP allows only one at that rate (2 are permitted at 0.56 kg ai/ha). At PHIs at or longer than the 35-day German and UK GAP and relating Swedish results to GAP in those countries, the residues which reflected GAP were ≤0.05 (11 results), 0.09 and 0.1 mg/kg in grain and 0.05, 0.09, 0.2, 0.3, 0.4, 0.6, 1 and 1.3 mg/kg in straw. Residues in whole plants were 2.7 and 3.8 mg/kg on the day of application. Most of the studies were reasonably well documented, although as with oats in several cases information was lacking on the analytical methods used or on analytical recoveries and representative chromatograms were not provided with the trials. Taking these results into account and with the support of those for barley and wheat, the Meeting estimated maximum residue levels of 0.5 mg/kg for rye grain and 5 mg/kg for rye straw and fodder, dry.

Leeks. Residues in whole leeks in eight supervised trials in the UK in 1982-3 (6 locations) were 0.1 to 0.4 mg/kg 20 to 38 days after 3-5 GAP applications of 0.75 ai/ha. The GAP PHI is 21 days. There appears to be little correlation between the number of applications or PHI (3-28 days) and residue levels. With one exception the interval from sampling to analysis was ≤6 months and the samples were reported to have been deep frozen. In the absence of more detailed information on sample

handling and methods of analysis (the data suggest that there were more than one), sample chromatograms, analytical recoveries and control values, the Meeting could not estimate a maximum residue level. If adequate supporting information can be provided to a future Meeting, the data may support an estimate of 0.5 mg/kg for leeks.

Onions. The Meeting did not use summary data submitted from Norway in the absence of detailed reports, which were acknowledged to be unavailable.

Sugar beets. Over 25 supervised trials (1982-89) were conducted in 6 Western European countries at GAP rates (0.38-1.1 kg ai/ha), with samples of sugar beet and sugar beet leaves taken at PHIs ranging from 0 to 113 days. GAP for sugar beets was reported only for Belgium, Denmark, Greece, Luxembourg and Switzerland but the trials, which were in Belgium, France, Greece, Italy, Sweden and Switzerland, cover the full range of reported GAP for Western Europe, in which the minimum PHI is 7 days (Greece). In all cases 6 or more days after the last application residues were reported as ≤0.05 mg/kg in the roots and ≤1 mg/kg (0.09 mg/kg median) in the leaves, with leaf residues approaching 1 mg/kg in several trials. Where they were provided, control values for both roots and leaves were <0.05 mg/kg. No data were available for sugar beet molasses or pulp.

The Meeting was not satisfied with the level of information provided in approximately half the trials on one or more of the following items/ sample handling and storage conditions, recovery data, control values and plot sizes. More often than not this was because only the analytical reports (without the corresponding field reports) were submitted.

In most cases the analytical method was identified as being one of those for which information was supplied to the Meeting, although no sample chromatograms were provided for sugar beets. They were provided for other crops in separate method validations. Analyses were generally conducted within 14 months of sampling, usually less. No storage stability studies were provided for sugar beet, although fenpropimorph has been shown to be stable for over a year in soil and wheat grain, straw and plants under frozen storage.

Although the Meeting found the overall submission to be only marginally acceptable, because several of the trials in different geographical areas and in different years were relatively well documented it concluded that maximum residue levels could be estimated. The Meeting considered the submission of validation of methods specifically for sugar beet roots and leaves, and of storage stability studies for a root crop to be highly desirable for a future JMPR evaluation in order to confirm the estimates. The Meeting estimated that fenpropimorph residues are unlikely to exceed 0.05 mg/kg (limit of determination) in sugar beet roots or 1 mg/kg in sugar beet leaves when GAP is followed.

Animal products. Of the crops for which maximum residue levels were estimated by the Meeting, those which may be fed to animals include the grain (0.5 mg/kg), straws and fodders of cereals (5 mg/kg), cereal grain forage (2 mg/kg) and sugar beet tops (1 mg/kg). No information was available on sugar beet molasses or pulp.

Assuming worst-case feeding situations for the above crops and maximum residue levels in them, maximum theoretical fenpropimorph levels in the feed would be 1.3 ppm for beef cattle, 1.7 ppm for dairy cattle and 0.35 ppm for poultry.

No conventional feeding trials data were provided to the Meeting. It is possible to make a crude estimate of total residues as fenpropimorph equivalents in cattle and poultry using the above estimates in conjunction with residue levels found in the metabolism studies on goats and hens. With these assumptions the total residues (mg/kg) in cattle/poultry would be muscle 0.01/0.003, fat 0.03/0.01, liver 0.3/0.03, kidneys 0.08/0.02, milk 0.02 and eggs 0.01.

There are several obstacles to recommending reliable MRLs for fenpropimorph in animal products. One is the lack of data on sugar beet pulp and molasses, although the studies provided suggest that residues in the roots, if present, may not exceed 0.01 mg/kg. A more serious obstacle is the lack of conventional feeding studies.

The guidance on livestock transfer studies in the 1993 JMPR report states that such studies are required (1) when detectable residues are found in feed items and metabolism studies indicate that significant residues (>0.01 mg/kg) may occur in edible tissues, and generally (2) where significant residues (generally >0.1 mg/kg) occur in crops or commodities fed to animals. Both situations occur with fenpropimorph. The guidance allows the possibility of using metabolism studies to serve as transfer studies when only low residue levels (<0.1 mg/kg) are found in feed items, but this does not apply to fenpropimorph. The situation does not lend itself to waiving the need for transfer studies.

Another complicating factor is the indication in metabolism studies that fenpropimorph *per se* is unlikely to occur in animal products with the possible exception of hen kidneys. The studies indicate that low residues of metabolites may occur, especially in liver and kidneys. None of the analytical methods provided to the Meeting is suitable for animal products and none determines metabolites (except BF 421-2 in soil). The Meeting was advised that an analytical method for the determination of fenpropimorph *per se* in animal tissue is available but it was not provided. There would be little point in recommending limits for the parent compound in animal products when its residues would not normally be expected.

No method has been provided for enforcing limits based on a definition of the residue which includes the most likely animal metabolites BF 421-1 (hydroxy-fenpropimorph) BF 421-2 (fenpropimorph acid) and BF 421-3 (hydroxymethyl-fenpropimorph acid). The Meeting was informed that a method for the determination of BF 421-2 is expected to be completed by the end of 1995, but it has not yet been decided whether feeding trials employing this method will be conducted.

The Meeting concluded that the data were insufficient to estimate maximum residue levels for animal products. For that purpose conventional transfer studies are needed for cattle and poultry, following Codex guidance and with analyses for the parent compound and likely metabolites by validated methods.

Fenpropimorph residues were reduced by 20 and 60% in Washington navel oranges and Hernandina clementines respectively held in storage for 30 days at 5°C. In the processed fractions residues increased slightly in the pulp over the same period, remained the same in the albedo and decreased by 10 and 46% respectively in the peel.

A summary report of a wheat processing study suggests fenpropimorph losses of >30% when processing wheat grain containing 0.07 mg/kg into bran, wholemeal or white flour. In this and three other summary reports bread baked from grain with residues of 0.05 to 0.08 mg/kg was reported to contain residues of <0.05 mg/kg. The Meeting could not confirm the results reported for the processed products in the absence of the detailed processing procedures. Processing studies on wheat grain containing residues near the estimated maximum level would be desirable for a clear picture of the extent of residue reduction.

With regard to the edible portions of food commodities, cereal grains are the main items for which MRLS are recommended. Trials showed that median residues in grain are likely to be <0.05 mg/kg and maximum residues unlikely to exceed 0.5 mg/kg. As noted above, summary reports suggest that residues in processed grain fractions and bread are likely to be less than in grain and probably not detectable (<0.05 mg/kg) in bread baked from grain containing expected median residues. This needs to be confirmed.

Although no MRLs are recommended for beans, leeks or citrus fruits, the data suggest that residues may not exceed 0.5 mg/kg from approved uses in leeks or 0.1 mg/kg in fresh beans. Although data were not provided for estimating a maximum residue level for citrus, the available information indicates that residues in citrus pulp are likely to be less than 10% of the residue in the whole fruit.

No information was provided on residues in commodities in commerce or at consumption.

RECOMMENDATIONS

The Meeting estimated the maximum residue levels listed below, which are recommended for use as MRLs.

Definition of the residue: fenpropimorph

Commodity		Recommended MRL, mg/kg	PHI on which based (days)
CCN	Name		
GC 0640	Barley	0.5	30
GC 0647	Oats	0.5	30
GC 0650	Rye	0.5	30
GC 0654	Wheat	0.5	30
AS 0640	Barley straw and fodder dry	5	30
AS 0647	Oats straw and fodder dry	5	30
AS 0650	Rye straw and fodder dry	5	30
AS 0654	Wheat straw and fodder dry	5	30
VR 0596	Sugar beet	0.05*	7
AV 1051	Fodder beet leaves or tops (sugar beet leaves or tops)	1	7

*At or about the limit of determination

FURTHER WORK OR INFORMATION

Desirable

1. Details (preferably in English) of the procedures used in the BASF wheat processing studies described in reports Nos. 79/10261, 79/10262, 79/10263 and 86/10411 for review at a future Meeting.

2. Conventional livestock and poultry feeding (transfer) studies with determination of fenpropimorph and the major metabolites identified in metabolism studies (e.g. BF 421-1, BF 421-2 and BF 421-3).

3. Validated analytical regulatory methods (including representative chromatograms) for the determination of fenpropimorph and its major metabolites in animal products.

4. Information on fenpropimorph residues in commodities in commerce or at consumption.

5. A study of the frozen storage stability of analytical samples of a root crop.

6. Validation of analytical methods used in the sugar beet trials.

REFERENCES

BASF 1979a. Residue Report, Summer wheat. Unpublished BASF Report No. 79/10263. Ciba fenpropimorph submission to 1994 JMPR Volume 2, tab 3.

BASF 1979b. Residue Report, Summer wheat. Unpublished BASF Report No. 79/10262. Ciba fenpropimorph submission to 1994 JMPR Volume 2, tab 2.

BASF 1979c. Residue Report, Summer wheat. Unpublished BASF Report No. 79/10261. Ciba fenpropimorph submission to 1994 JMPR Volume 2, tab 1.

BASF 1982. Report on Behaviour of Fenpropimorph in Water (Hydrolysis) at High Temperatures. Unpublished BASF Report No. 205.3.65-041/3271, April 1983 (Included/ "Behavior of Pesticides in Water" 205.3.65-041/3271 dated January 12, 1982). Ciba fenpropimorph submission to 1994 JMPR Volume 1 Section 1, tab 1.

BASF 1985. Residue Report, Corbel Top Summer wheat. Unpublished BASF Report No. 86/10411. Ciba JMPR fenpropimorph submission Volume 2, tab 4.

BASF 1988a. Determination of the Vapor Pressure of Fenpropimorph. Unpublished BASF report APE/CF-Li 475. Ciba fenpropimorph submission to 1994 JMPR Volume 1 Section 1, tab 5.

BASF 1988b. Bestimmung der Löslichkeit von Fenpropimorphhydrochlorid in Wasser. Unpublished BASF Report No. 2593, project code PCP 00507. Ciba fenpropimorph submission to 1994 JMPR Volume 1 Section 1, tab 3.

BASF 1988c. Wasserlöslichkeit von Fenpropimorph im Neutralbereich and bei pH 9-11. Unpublished BASF Report No . 2596, project code PCP 00511. Ciba fenpropimorph submission to 1994 JMPR Volume 1 Section 1, tab 4.

Beutel, P. 1979. Analytical determination of residues of the fungicide fenpropimorph (Ro 14-3169/000 = BAS 108 406 F) in green plants, straw, grain, soil and water. Unpublished BASF GPE/R Method 137 (Maag method 840-MD-01); 041/0245. Ciba fenpropimorph submission to 1994 JMPR Volume 5 tab 1.

Beutel, P. and Tilting, N. 1987. Fenpropimorph, wheat: forage, spindles, stalk, straw, grain. Rape: forage, seeds. Brussels sprouts, tangerines, oranges. Gas-chromatographic determination. Unpublished BASF Method 241; Registration Doc. No. BASF 87/10142. Ciba fenpropimorph submission to 1994 JMPR Volume 5 tab 2.

Ciba 1992. Report on General Physico-chemical Properties. Unpublished Ciba summary report (Project No EA 166768).

Ciba 1994. Ciba and BASF fenpropimorph supervised field trials reports submitted by Ciba-Geigy Limited in Volume 7 (barley, oats, rye, beans, sugar beet) and Volume 8 (wheat) as part of an 8-Volume submission to 1994 JMPR.

Diekmann, H., Stockmaier, M., Kreuzig, R. and Bahadir, M. 1993. Simultaneous determination of fenpropimorph and the corresponding metabolite fenpropimorph acid in soil. Fresenius J. Anal. Chem. 345, 784-6. Ciba fenpropimorph submission to 1994 JMPR Volume 5 tab 3.

Hamm, R. 1982. Aquatic degradation of ^{14}C-BAS 421 F (fenpropimorph). Unpublished BASF laboratory report 1815. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 5.

Hänni, R. and von der Mühll. 1981. Analytical Determination of Residues of the Fungicide Fenpropimorph (Ro 14-3169) in green plants, grain, straw, soil and water. Unpublished BASF method No. 156; Maag method 840-MD-02; Registration No. 041/24145. Ciba fenpropimorph submission to 1994 JMPR Volume 5 tab 4.

Hawkins, D., Jackson, A., Roberts, N. and Cameron, D. 1980a. Residues of radioactivity in tissues and milk after oral administration of ^{14}C-BAS 421 F to goats. Unpublished Huntington Research Centre report no. FSF 348/80539. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 6.

Hawkins, D., Jackson, A., Roberts, N. and Cameron, D. 1980b. Excretion of radioactivity after oral administration of ^{14}C-BAS 421 F to goats. Unpublished Huntington Research Centre report no. FSF 348/80545. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 7.

Herrchen, M. 1988a. Water Photolysis of BAS 421 F at

pH = 5. Unpublished BASF Registration Doc. No. BASF 88/0489. Study No. P86-C009. Ciba fenpropimorph submission to 1994 JMPR Volume 1 Section 1, tab 7.

Herrchen, M. 1988b. Soil photolysis of fenpropimorph. Unpublished BASF Registration Doc. No. BASF 88/0433. Study No. P86-C010. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 8.

Hesse, B. and Tilting, N. 1991. Prüfung des Abbauverhaltens von Fenpropimorph im Boden unter Feldbedingungen. Unpublished BASF Registration Doc. No. 91/10396, Report No. 3253. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 9.

Hesse, B. and Tilting, N. 1992. Prüfung des Abbauverhaltens von Fenpropimorph im Boden unter Feldbedingungen. Unpublished BASF Registration Doc. No. 92/11222, Report No. 3549. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 10.

Huber, R. 1979a. Investigations on the metabolism of fenpropimorph (Registration No. 108406, BAS 421-F) in wheat. Unpublished BASF Report No. 1672, Maag. doc. 041/0718. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 11.

Huber, R. 1979b. Stage on the investigations on the metabolism of fenpropimorph in soil. Unpublished BASF Report No. 1684, Maag. doc. 041/0719. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 12.

Huber, R. 1980. Investigations on the mineralization of fenpropimorph in soil. Unpublished BASF Registration Doc. No. 041/3549, Laboratory communication No. 889. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 13.

Lafuente, M. and Tadeo, J. 1987. GLC multiresidue analysis of postharvest fungicides in citrus fruit. Fresenius Z. Anal. Chem. 328 (1-2), 105-7. Ciba fenpropimorph submission to 1994 JMPR Volume 5 tab 5.

Lafuente, M., Tadeo, J. and Tuset, J. 1986. Gas chromatographic determination of fenpropimorph residues in citrus fruit. J. Assoc. Off. Anal. Chem. 69 (5), 859-62. Ciba fenpropimorph submission to 1994 JMPR Volume 5 tab 6.

Keller, W. 1986. Determination of the n-Octanol Water Partition Coefficient of Fenpropimorph (Flask shaking method). Unpublished BASF report (lab. com. no. BASF-LC 1078-1). Ciba fenpropimorph submission to 1994 JMPR Volume 1 Section 1, tab 2.

Olthof, P. Information of The Netherlands on pesticides to be considered by the JMPR 1994. Fenpropimorph. Olthof to Ives, 2/22/94).

Pryde, A. and Etterli, M. 1979. Investigation of the relative contribution of the systemic and gas phase activities to the total activity of ^{14}C-Ro 14-3169/001 formulated as ACR 3320 in barley plants using chemical and autoradiographic techniques. Unpublished Internal Report 041/0495. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 14.

Pryde, A. and Etterli, M. 1980. Crop rotation studies with radioactive fenpropimorph (Ro 14-3169/001). Unpublished Internal Report 041/0892. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 15.

Pryde, A., Etterli, M. and Oesterfelt, G. 1979. Metabolism of ^{14}C-Ro14-3169/005 in the rat. Unpublished Hoffmann-La Roche report.

Pryde, A., Etterli, M. and Oesterfelt, G. 1980. Metabolism of ^{14}C-Ro14-3169/005 in the rat/ Additional results. Unpublished Hoffmann-La Roche report.

Ritter, A. 1989a. Distribution, degradation and excretion of ^{14}C-BAS 421 F after repeated oral administration to lactating goats. Unpublished Research Consulting Company report no. 081303. Ciba fenpropimorph submission to 1994 JMPR Volume 2 Section 2, tab 16.

Race, J. 1994. Letter to N. Ives, February 26, 1994 with attachments, including letter (F. Hellstrom, Norwegian Food Control Authority, August 27, 1993) to B. Murray explaining that there were no detailed reports for the residue trials summaries submitted.

Ritter, A. 1989b. Distribution, Excretion, and Metabolism of ^{14}C-BAS 421F After Repeated Oral Administration to Laying Hens. Unpublished Ciba project 081314. Ciba fenpropimorph submission to 1994 JMPR Volume 3, Section 2, Tab 17.

Ritter, A. 1990. Degradation of ^{14}C-Ro 14-3169/107 in two aquatic systems under aerobic conditions. Unpublished RRC Umweltchemie AG Project 099955. Ciba fenpropimorph submission to 1994 JMPR Volume 3 Section 2, tab 18.

Rüdel, H. 1988. Hydrolysis Studies on BAS 421 F at pH 3, 5, 7 and 9. Unpublished BASF Study No. P86-C011. Ciba fenpropimorph submission to 1994 JMPR Volume 3 Section 2, tab 19.

Rüdel, H. 1990. Investigations on the metabolism of fenpropimorph (re. Nr. 108406, BAS 421 F) in wheat. Unpublished BASF Study No. P86-CO12. Ciba fenpropimorph submission to 1994 JMPR Volume 3, tab 20.

Tadeo, J. and Lafuente, M. 1987. Determination of fenpropimorph in citrus fruit by reversed-phase high performance liquid chromatography. J. Chromatog., 391, 338-42. Ciba fenpropimorph submission to 1994 JMPR Volume 5, tab 7.

Tilting, N. 1987. Fenpropimorph, Wasser, gaschromatogarphische Bestimmung. Unpublished BASF method No. 271. Ciba fenpropimorph submission to 1994 JMPR Volume 5, tab 8.

Tilting, N. 1989. GC-bestimmung von Fenpropimorphsäure im Boden. Unpublished BASF method 298. BASF Registration Doc. 89/10208. Ciba fenpropimorph submission to 1994 JMPR Volume 5, tab 9.

Tilting, N. 1993. Two years storage stability study of fenpropimorph residues in wheat and soil. Unpublished BASF Registration Doc. No. 93/10781; Report No. 3678. Ciba fenpropimorph submission to 1994 JMPR Volume 3, tab 21.

Van Dijk, A. and Vogel, W. 1989. ^{14}C-Ro 14-3169/ Absorption, distribution, excretion and metabolism after single intravenous, single oral and repeated oral administration to the rat. Project No. 06341. Research and Consulting Co. unpublished report. Ciba fenpropimorph submission to 1994 JMPR Volume 4, tab 22.

von der Mühll, F. and Gätzi, M. 1979. ^{14}C-Ro-14-3169/005/ Rat balance study after oral administration. Unpublished Hoffmann-La Roche Internal Report 041/0169. Ciba fenpropimorph submission to 1994 JMPR Volume 4, tab 23.

von der Mühll, P.A., Pryde, A., Gätzi, M. and Etterli, M. 1980. Soil field dissipation, metabolism and leaching study with radioactive fenpropimorph. Unpublished Maag Ltd. Report 204-12-173; Internal Report 041/1176. Ciba fenpropimorph submission to 1994 JMPR Volume 4, tab 24.

Zoonen, P. and Harten, D. 1988. Determination of fenpropimorph residues in grains by reversed phase high performance liquid chromatography followed by confirmation with capillary gas chromatography with a nitrogen-phosphorus detector, submitted for publication in J. Chromatog. BASF Registration Doc. No. 88/10515. Ministry of Welfare, Health and Cultural Affairs, Rijswijk-Netherlands/ Analytical Methods for Residues of Pesticides, 5th Ed.(1988). Ciba fenpropimorph submission to 1994 JMPR Volume 5, tab 10.

FENPYROXIMATE

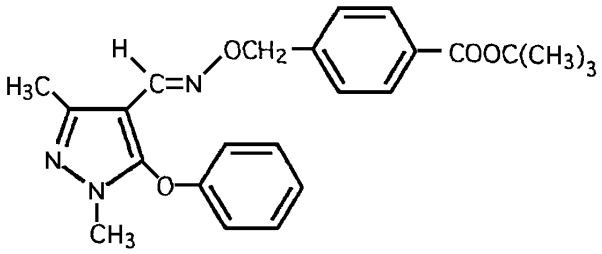
IDENTITY

ISO common name: Fenpyroximate (draft)
Chemical name
IUPAC: *tert*-butyl (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate
CA: (*E*)-1,1-dimethylethyl 4-[[[[(1,3-dimethyl-5-phenoxy-1*H*-pyrazol-4-yl)methylene]amino]oxy]methyl]benzoate

CAS No.: 111812-58-9

Synonyms: Danitron, Kiron, Naja, Dynamite, NNI-850

Structural formula:



Molecular formula: $C_{24}H_{27}N_3O_4$
Molecular weight: 421.50

Physical and chemical properties

Pure active ingredient

Vapour pressure at 25°C:	5.6×10^{-8} mm Hg	
n-Octanol/water partition coefficient:	log P_{ow} = 5.01	
Solubility in water at 25°C:	pH 5	0.021 mg/l
	pH 7	0.023 mg/l
	pH 9	0.030 mg/l

Technical material

Physical state:	solid
Colour:	off-white to pale yellowish
Odour:	practically odourless
Purity:	95.9-99.8%
Density:	1.237-1.257 g/cm^3
Melting point:	99.3-101.7 °C

Solubility in organic solvents at 25°C:	n-Hexane	3.5 g/l
	Methanol	15.3 g/l
	Ethanol	16.5 g/l
	Acetonitrile	37.4 g/l
	Acetone	150 g/l
	Ethyl acetate	201 g/l
	Benzene	207 g/l
	Toluene	268 g/l
	Chloroform	1197 g/l
Flammability:	Not applicable	
Hydrolysis:	Half-life (25°C) at	pH 5: 180 days pH 7: 226 days pH 9: 221 days
Photolysis:	Half-life at pH 7: 1.5 hours (in aqueous solution irradiated with a xenon lamp of 603 watts, 290-800 nm)	
Storage stability:	Stable for more than 1 year	

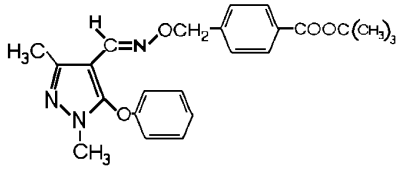
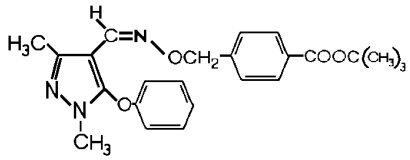
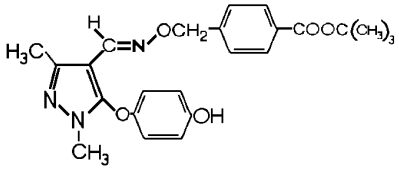
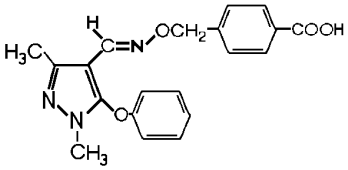
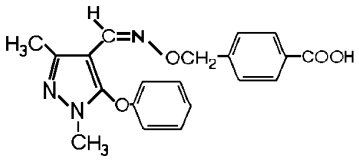
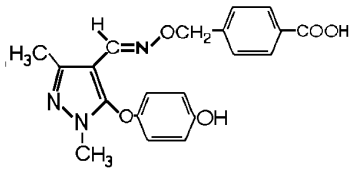
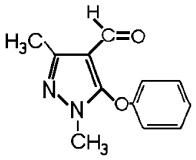
Formulation

Fenpyroximate is formulated as a 5% suspension concentrate.

METABOLISM AND ENVIRONMENTAL FATE

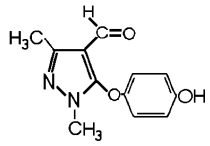
The labelled compounds [*pyrazole*-^{14}C] and [*benzyl*-^{14}C]fenpyroximate were used in a series of studies on metabolism in rats and plants (citrus, apples and grapes), and degradation in soil and water. The chemical names and structures of fenpyroximate and its metabolites are shown in Table 1.

Table 1. Chemical names and structures of fenpyroximate and its metabolites

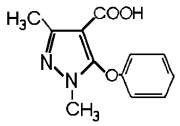
tert-butyl (*E*)-Æ-(1,3,-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate (fenpyroximate)		
tert-butyl (*Z*)-Æ-(1,3,-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate (M-1)	(A)	
tert-butyl (*E*)-4-([1,3,-dimethyl-5-(4-hydroxyphenoxy)pyrazol-4-yl)methyleneamino-oxymethyl)benzoate (M-2)	(B)	
(*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid	(C)	
(*Z*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid	(D)	
(*E*)-Æ-(1,3-dimethyl-5-(4-hydroxy-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid (M-5)	(E)	
1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde	(F)	

fenpyroximate

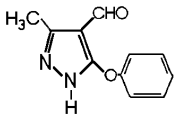
1,3-dimethyl-5-(4-hydroxyphenoxy)pyrazole-4-carbaldehyde (G)



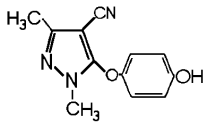
1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid (H)



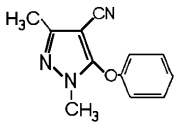
3-methyl-5-phenoxypyrazole-4-carbbaldehyde (M-9) (I)



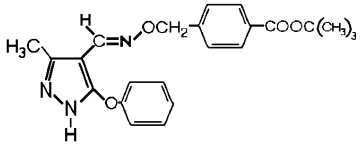
1,3-dimethyl-5-(4-hydroxyphenoxy) pyrazole-4-carbonitrile (M-10) (J)



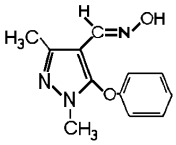
1,3-dimethyl-5-phenoxypyrazole-4-carbonitrile (K)



tert-butyl (*E*)-Æ-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate (L)

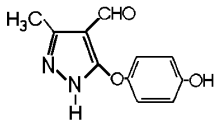


(*E*)-1,3-dimethyl-5-phenoxy-pyrazole-4-carbaldehyde oxime (M-13) (M)



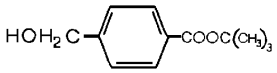
fenpyroximate

(N)



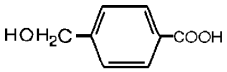
3-methyl-5-(4-hydroxyphenoxy)-pyrazole-4-carbaldehyde (M-14)

(O)



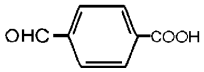
tert-butyl Æ-hydroxy-*p*-toluate (M-15)

(P)



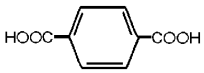
Æ-hydroxy-*p*-toluic acid (M-16)

(Q)



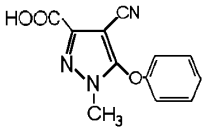
4-formylbenzoic acid (M-17)

(R)



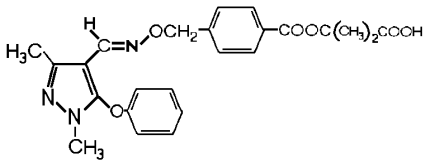
terephthalic acid (M-8)

(S)



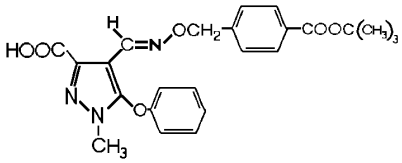
4-cyano-1-methyl-5-phenoxy-pyrazole-3-carboxylic acid (M-21)

(T)



(*E*)-2-[4-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethylene-amino-oxymethyl)benzoyloxy]-2-methylpropionic acid (M-22)

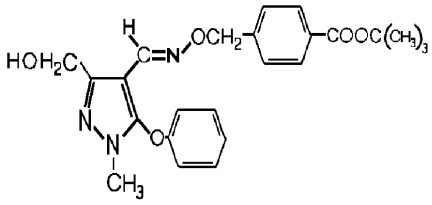
(U)



(*E*)-4-[-4(*tert*-butoxycarbonyl)benzloxyiminomethyl]-1-methyl-5-phenoxypyrazole-3-carboxylic acid (M-19)

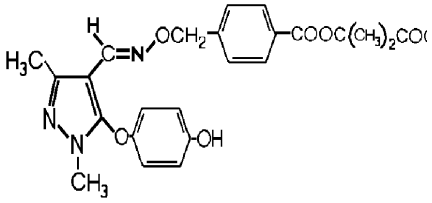
tert-butyl (*E*)-Æ-(3-hydroxymethyl-1-methyl-5-phenoxyprazol-4-ylmethyleneamino-oxy-*p*-toluate (M-20)

(V)



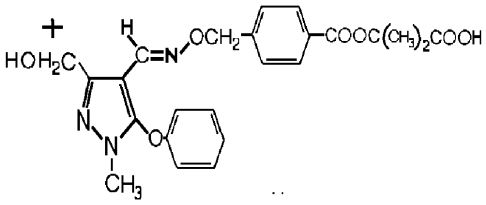
(*E*)-2-[-[1,3-DIMETHYL-5-(4-hydroxyphenoxy)pyrazole-4-ylmethyleneamino-oxymethyl]benzoyloxy]-2-methyl-propionic acid

(W)



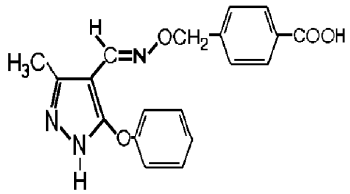
(*E*)-2-[4-[(3-hydroxymethyl-1-methyl-5-phenoxypyrazol-4-yl)-methyleneamino-oxymethyl]-benzoyloxy]-2-methylpropionic acid

(X)



(*E*)-Æ-(1,3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid

(Y)



Animal metabolism

A metabolic study was undertaken with the objective of determining the distribution, elimination and biotransformation of [*pyrazole*-^{14}C]fenpyroximate administered orally to male and female rats at various doses.

The rats were divided into three groups (A, B, C). Group A was dosed orally with [*pyrazole*-^{14}C]fenpyroximate suspended in 1% aqueous Tween 80 at 2 mg/kg bw. Group B received 14 consecutive daily doses of unlabelled fenpyroximate followed by a single dose of radiolabelled material at 2 mg/kg bw. Group C was dosed orally with 400 mg/kg bw of [*pyrazole*-^{14}C]fenpyroximate suspended in aqueous Tween 80 solution.

In a preliminary experiment it was determined that negligible amounts of radioactivity were expired as CO_2 or volatile organic compounds after the oral administration of [*pyrazole*-^{14}C]fenpyroximate at 2 mg/kg bw.

After dosing with labelled fenpyroximate, urine and faeces were collected at intervals up to 168 hours, when the animals were killed for assay of the radioactivity in various tissues.

After the administration of fenpyroximate at 2 mg/kg, radioactivity was rapidly excreted. After 7 days, 70-85% of the dose was eliminated in the faeces and 12-18% in the urine. Residues at 7 days in fat were 0.025 and 0.011 ì g/g fenpyroximate equivalents in males and females respectively. Residues in liver were 0.003 ì g/g in both males and females. No residues were detected in other tissues. Similar results were obtained by multiple dosing of the unlabelled compound followed by a single dose of labelled fenpyroximate at 2 mg/kg. Residues expressed as fenpyroximate equivalents were 0.016 and 0.008 ì g/g in the fat and 0.005 and 0.003 ì g/g in the liver of males and females respectively. Slower excretion was observed after a single administration at 400 mg/kg, but after 168 hours 75-77% of the dose was eliminated in the faeces and 11-12% in the urine. Residues in the tissues were generally low at 168 hours, and parts of the gastrointestinal tract showed the highest concentrations of radioactivity at 1-4% of the dose. The delayed movement of fenpyroximate through the gastrointestinal tract at 400 mg/kg is probably due to its toxic effect.

The major urinary metabolites were 1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid (H) and 4-cyano-1-methyl-5-phenoxypyrazole-3-carboxylic acid (S). A large amount of (apparently unabsorbed) fenpyroximate was present in the faeces; the major faecal metabolites were (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid (C) and (*E*)-2-[4-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxymethyl)benzoyloxy]-2-methylpropionic acid (T).

Residues in the tissues were generally very low at 168 hours, with the highest concentrations of radioactivity in all groups in the liver, kidneys, fat and urinary bladder. In all groups in which radioactivity was detectable, the concentration in the plasma was about twice that in the blood, indicating that nearly all of the radioactive material in the blood was in the plasma.

Urine, plasma, cage rinses and washes, and carbon dioxide trapping solutions were analyzed directly by LSC. Urine and faeces were extracted with various solvents to determine the total extractable residues, and the metabolites in the extracts were identified by TLC and HPLC (Sharp, 1991a).

A similar study was carried out with [*benzyl*-^{14}C]fenpyroximate. Similar patterns of excretion and tissue distribution were observed. The major urinary metabolite was terephthalic acid (R). As with [*pyrazole*-^{14}C]fenpyroximate large amounts of the parent compound were present in the faeces. Major metabolites were C and (*Z*)-Æ-(1,3-dimethyl-5-phenoxypyrazole-4-ylmethyleneamino-oxy)-*p*-toluic acid (D) (Sharp, 1991b).

Further studies to elucidate the metabolic fate in rats were carried out with fenpyroximate labelled in the pyrazole ring, the phenoxy group and the *tert*-butyl group.

Fenpyroximate is metabolized by oxidation of the *tert*-butyl and pyrazole-3-methyl groups, *p*-hydroxylation of the phenoxy moiety, *N*-demethylation, hydrolysis at the ester and methyleneamino-oxy bonds, and conjugation. *E/Z* isomerization also occurs, giving the faecal metabolites A and D.

The proposed metabolic pathways of fenpyroximate in rats are shown in Figure 1, which includes the 3 metabolites W, X and Y which were subsequently identified by NMR spectrometry (Nishizawa *et al.*, 1993).

Plant metabolism

Metabolism studies were carried out with ^{14}C-labelled fenpyroximate, solutions of the product being sprayed on citrus, apple trees and grape vines.

Citrus. Satsuma tangerine trees were sprayed with [*pyrazole*-^{14}C]fenpyroximate at application rates of 22. 4 ± 1. 5 mg/tree (group 1) and 33.5 ± 0.5 mg /tree (group 2) at a concentration of 5 g/hl. Group 1 trees received 61.9 ± 4.3 ì Ci/tree and fruit were harvested after 0, 3, 7, 14 and 28 days. Group 2 trees received 703.5-705.9 ì Ci/tree and the fruit were harvested at maturity, 137 days after treatment. Two untreated trees served as controls. Leaves, fruit and soil samples were collected. The fruit were separated into pulp and peel, each sample was homogenized and the residues quantitatively determined by combustion and liquid scintillation spectroscopy. Table 2 shows the results (Krautter *et al.*, 1989).

Table 2. Mean residues of ^{14}C expressed as fenpyroximate in tangerine plant tissues and soil (Krautter *et al.*, 1989).

Sample	^{14}C as mg/kg pyroximate at interval, days					
	Group 1					Group 2
	0	3	7	14	28	137
Leaves	5.33	5.54	3.37	2.27	1.78	1.37
Peel	0.49	0.63	0.52	0.48	0.49	0.37
Fruit (pulp)	N.D.[1]	N.D.[1]	N.D.[1]	N.D.[1]	N.D.[1]	N.D.[2]
Soil	5.50	8.40	7.04	5.91	7.42	4.59

[1] LOD 0.03 mg/kg
[2] LOD 0.004 mg/kg

The samples were investigated further at another laboratory (Izawa *et al.*, 1990). The radioactivity in the fruit pulp was too low for further analysis. Extracts of leaves and peel were analysed by thin-layer co-chromatography and autoradiography (TLC-ARG). The level of fenpyroximate in the peel was 0.44 mg/kg at day 0 and 0.12 mg/kg at day 137: the half-life was 38.4 days. In the leaves the residues at days 0 and 137 were 4.88 and 0.24 mg/kg respectively, and the half-life was 8.8 days. The major metabolites in the leaves and peel were the *Z*- isomer of fenpyroximate (A) and *tert*-butyl (*E*)-4-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxymethyl)benzoate (demethyl-fenpyroximate, L). The results are shown in Table 3 (Izawa *et al.*, 1990).

Figure 1. Proposed metabolic pathways of fenpyroximate in rats.

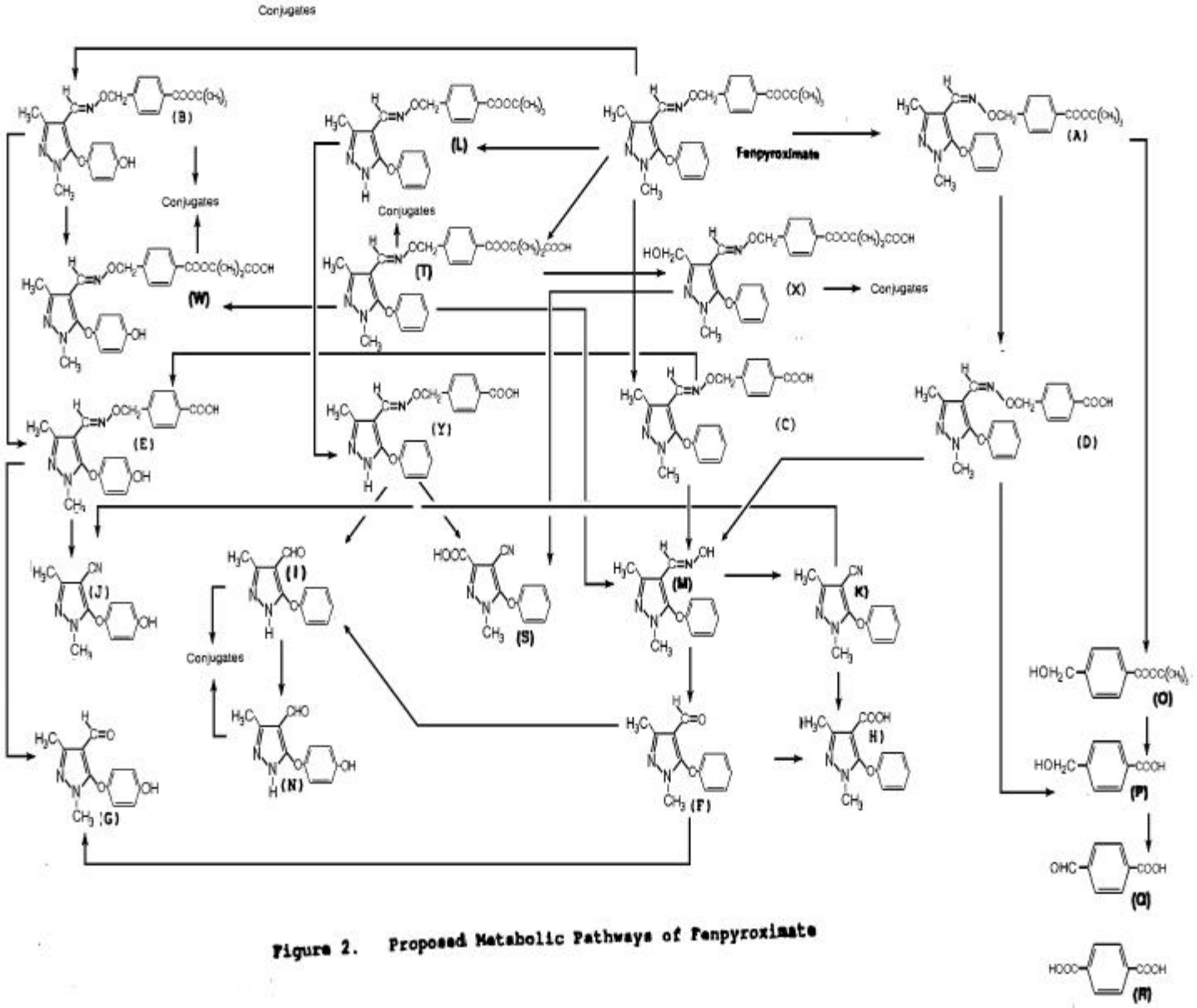


Figure 2. Proposed Metabolic Pathways of Fenpyroximate

fenpyroximate

fenpyroximate

Table 3. Radioactivity in citrus leaves and peel after [^{14}C]fenpyroximate application (Izawa *et al.*,1990).

Sample	^{14}C expressed as mg/kg fenpyroximate (fresh weight) at interval, days					
	Group 1					Group 2
	0	3	7	14	28	137
Leaves, total	5.33	5.54	3.37	2.27	1.78	1.37
Extractable	5.28 (99.1)	4.89 (88.3)	2.58 (76.6)	1.53 (67.4)	1.33 (74.7)	1.05 (76.6)
Unextractable	0.05 (0.9)	0.65 (11.7)	0.79 (23.4)	0.74 (32.6)	0.45 (25.3)	0.32 (23.4)
Peel, total	0.49	0.63	0.52	0.48	0.49	0.36
Extractable	0.49 (100)	0.62 (98.4)	0.50 (96.2)	0.46 (95.8)	0.46 (93.9)	0.33 (91.9)
Unextractable	0 (0)	0.01 (1.16)	0.02 (3.8)	0.02 (4.2)	0.03 (6.1)	0.03 (8.1)

Values in parentheses represent % of total radioactivity in each sample

Table 4. Concentration of fenpyroximate and its metabolites in citrus peel and leaves after ^{14}C-fenpyroximate application.

Compound	Days after application					
	0	3	7	14	28	137
Peel						
Fenpyroximate	0.44 (90)	0.52 (84)	0.42 (84)	0.32 (70)	0.30 (65)	0.12 (36)
A	0.05 (10)	0.03 (5)	0.02 (4)	0.05 (11)	0.02 (4)	0.02 (6)
K	nd	nd	nd	nd	nd	0.01 (3)
L	nd	nd	nd	nd	0.02 (4)	0.06 (18)
Leaves						
Fenpyroximate	4.88 (92)	3.37 (69)	1.01 (39)	0.56 (37)	0.51 (38)	0.24 (23)
A	0.23 (4)	0.29 (6)	0.15 (6)	0.23 (15)	0.25 (19)	0.13 (12)
I	n.d	0.20 (4)	0.13 (5)	0.08 (5)	<0.06	<0.01
K	n.d	<0.06	<0.06	<0.06	<0.06	<0.01
L	0.12 (2)	0.44 (9)	0.27 (10)	0.09 (6)	<0.06	0.08 (8)

Values in parentheses represent % of the extractable radioactivity

The other minor metabolites in the peel, (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid (C), 1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde (F), 1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid (H), 3-methyl-5-phenoxypyrazole-4-carbaldehyde (I), (*E*)-1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde oxime (M), 3-methyl-5-(4-hydroxyphenoxy)-pyrazole-4-carbaldehyde (N), (*E*)-4-[4-(-*tert*-butoxycarbonyl)benzyloxyiminomethyl]-1-methyl-5-phenoxypyrazole-3-carboxylic acid (U) and *tert*-butyl (*E*)-Æ-(3-hydroxymethyl-1-methyl-5-phenoxypyrazole-4-ylmethyleneamino-oxy)-*p*-toluate (V) were detected at concentrations of less than 0.01 mg/kg at day 137 (Izawa *et al.*, 1991a).

In another study with [*benzyl*-^{14}C]fenpyroximate, satsuma mandarin trees were sprayed at the rate of 1 mg/tree (experiment 1 10 ì Ci/tree; experiment 2 35 ì Ci/tree). Fruit and leaves were collected

after 0, 3, 7, 14 and 28 days in experiment 1 and 98 days in experiment 2. The radioactivity in all pulp samples was less than 0.01 mg fenpyroximate equivalents/kg. In the peel the residues of fenpyroximate were 1.12 mg/kg just after application and 0.09 mg/kg at day 98, and in the leaves 9.75 mg/kg at day 0 and 0.21 mg/kg at day 98. The concentrations of the extractable and unextractable radioactivity in the peel and of the identified metabolites in the extracts are shown below (Izawa *et al.*, 1991b).

Table 5. Concentration of fenpyroximate and metabolites in citrus peel after [*benzyl*-^{14}C]fenpyroximate application.

Compound or fraction	^{14}C expressed as mg/kg fenpyroximate (fresh weight) at interval, days				
	0	7	14	28	98
Fenpyroximate	1.12 (100)	0.81 (83)	0.83 (79)	0.53 (70)	0.09 (53)
Metabolite A	nd	0.04 (4)	0.05 (5)	0.02 (3)	0.01 (6)
Metabolite L	nd	0.12 (12)	0.12 (11)	0.10 (13)	0.04 (24)
Extractable	1.12	0.98	1.05	0.76	0.17
Unextractable	0.01	0.04	0.11	0.11	0.04

Values in parentheses represent % of the extractable radioactivity

The other minor metabolites, B, C, O, Q, U and V were less than 0.01 mg/kg at day 98.

From these results, fenpyroximate was shown to be metabolized in citrus trees by hydrolysis of the ester and methyleneamino ether links, *N*-demethylation, oxidation, and conjugation of the polar metabolites (Izawa *et al.*, 1991).

Apple trees were sprayed with a 5% SC formulation of [*pyrazole*-^{14}C]fenpyroximate at the maximum recommended rate of 7.5 g ai/hl (37.5 g ai/ha/m crown height) and 908.6 ì Ci/tree (Galicia & Wyss-Benz, 1992). Fruit and leaves were collected 0, 7, 14, 28 and 57 days (harvest) after application. The total radioactivity in the fruit was 0.128 mg/kg fenpyroximate equivalents at day 0 and 0.032 mg/kg at day 57. In leaves, the total radioactivity decreased from 10.33 mg/kg at day 0 to 0.51 mg/kg at day 57. The total radioactivity in the juice was 0.003 mg/kg at day 57. Unchanged fenpyroximate and metabolite A were the major residues in both fruit and leaves. The concentrations of radioactivity in various fractions derived from the fruit are shown in Table 6.

The study was reported as being in compliance with GLP according to the OECD, Switzerland, and the EPA.

Table 6. Concentration of fenpyroximate and metabolites in apples after treatment with [*pyrazole*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total in fruit	0.128	0.108	0.081	0.061	0.032
Fenpyroximate	0.119	0.094	0.062	0.043	0.015
Metabolite A	0.007	0.009	0.009	0.008	0.005
Unknown 1	-	-	-	0.001	-
Unknown 2	-	-	-	0.004	0.001
Unknown 3	-	-	0.003	-	-

fenpyroximate

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Unknown 9	-	0.001	-	-	-
Aqueous phase	-	0.002	0.003	0.003	0.005
Juice	0.001	0.001	0.001	0.002	0.003
Unextractable	-	-	-	0.001	0.001

In leaves, the residues of fenpyroximate and A were 0.221 and 0.091 mg/kg at day 57 respectively, and 5 unidentified metabolites were found in washed and extracted fractions, but none of the minor metabolites were present at harvest. The proposed degradation pathway of fenpyroximate (pyrazole labelled) in apples is as follows.

Parent ----------➢ A
(Isomer of parent)
↓
Unknown metabolites

The metabolism of [*benzyl*-^{14}C]fenpyroximate by apples investigated with a similar experimental design (Wyss-Benz & Mamouni, 1992a). [^{14}C]fenpyroximate was applied at the rate of 37.5 g ai/ha/m crown height and 955 ì Ci/tree. The total radioactivities at day 0 were equivalent to 0.12 mg fenpyroximate/kg in fruits and 12.2 mg/kg in leaves, decreasing to 0.036 and 0.628 mg/kg respectively at day 57. The radioactivity in the juice was equivalent to 0.02 mg/kg at day 57. The major residual products were unchanged fenpyroximate and metabolite A in both fruits and leaves. The concentrations of radioactivity in the various fractions are shown in Table 7.

Table 7. Concentration of fenpyroximate and metabolites in apples after treatment with [*benzyl*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total in fruit	0.120	0.140	0.110	0.075	0.036
Fenpyroximate	0.109	0.113	0.086	0.053	0.017
Metabolite A	0.005	0.017	0.013	0.011	0.007
Unknown 1	-	0.001	-	-	0.001
Unknown 2	0.004	0.004	0.003	0.003	0.001
Aqueous phase	0.002	0.004	0.004	0.003	0.007
Juice	-	-	0.001	0.001	0.002
Unextractable	-	-	0.001	0.001	0.002

In leaves, the residues of fenpyroximate and A were 0.219 and 0.162 mg/kg respectively at day 57, and 7 unknown metabolites were found.

Grapes. A 5% SC formulation of [*pyrazole*-^{14}C]fenpyroximate was applied by hand spraying to two vines in the field at the maximum recommended field rate of 7.5 g ai/hl and 731 ì Ci/vine. Samples of bunches and leaves were taken 0, 7, 14, 28 and 57 days (harvest) after application. The samples were rinsed with acetone/water and the radioactivity determined by LSC. Bunches were separated into grapes and stems, grapes were homogenized and separated into juice and cake, and washings as well as extracts were analysed. The highest total radioactivity in grape bunches was 0.195 mg/kg fenpyroximate equivalents at day 7, decreasing to 0.081 mg/kg at day 57. Leaves accounted for 6.234 mg/kg at day 0 and 0.971 mg/kg at day 57. The concentrations of ^{14}C residues in grape bunches and individual fractions are shown in Table 8.

Table 8. ^{14}C residues in grape bunches treated with [*pyrazole*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total	0.097	0.195	0.102	0.051	0.081
Fenpyroximate	0.096	0.140	0.067	0.028	0.031
Metabolite A	-	0.004	0.004	0.002	0.004
Unknown 1	-	0.001	-	0.002	0.002
Unknown 3	-	0.015	0.010	0.002	0.016
Unknown 5	-	0.001	0.001	-	0.001
Unknown 6	-	-	-	-	0.001
Unknown 8	-	-	-	-	0.001
Aqueous phase	0.001	0.014	0.011	0.008	0.010
Juice	-	0.005	0.005	0.004	0.007
Unextractable	-	0.004	0.004	0.003	0.006

In the leaves, the residues of fenpyroximate and A were 0.326 and 0.052 mg/kg respectively at day 57. Seven unknown metabolites found at day 57 were in the range 0.002-0.14 mg/kg (Wyss-Benz & Mamouni, 1992b).

In another study with the same experimental design but using [*benzyl*-^{14}C]fenpyroximate the labelled compound was applied to vines in the field at the rate of 37.5 g ai/ha/m crown height and 770 ì Ci/vine. Samples were taken at days 0, 7, 14, 28 and 57 (harvest). The total radioactivities at day 0 were 0.086 mg/kg fenpyroximate equivalents in grape bunches and 7.49 mg/kg in leaves, decreasing to 0.060 and 1.16 mg/kg respectively at day 57. The concentrations of radioactivity in various fractions derived from the fruit are shown in Table 9.

Table 9. ^{14}C residues in grape bunches treated with [*benzyl*-^{14}C]fenpyroximate.

	mg fenpyroximate equivalents/kg fresh fruit at interval, days				
	0	7	14	28	57
Total	0.086	0.144	0.075	0.087	0.60
Fenpyroximate	0.079	0.109	0.049	0.053	0.027
Metabolite A	0.004	0.013	0.007	0.016	0.006
Unknown 1	-	-	-	-	0.001
Unknown 2	-	0.001	0.002	0.001	0.002
Unknown 3	-	0.008	0.004	0.006	0.006
Unknown 5	-	0.001	-	-	0.001
Unknown 6	-	0.001	0.001	0.002	-
Aqueous phase	0.001	0.005	0.005	0.007	0.006
Juice	-	0.004	0.005	0.006	0.005
Unextractable	-	0.001	0.001	0.002	0.002

In the leaves, the residues of fenpyroximate and A were 0.64 and 0.054 mg/kg respectively at day 57. Eight metabolites were found in the range 0.005-0.132 mg/kg. The juice was not extracted because the level of radioactivity was so low, <0.008 mg/kg (Wyss-Benz & Mamouni, 1992c).

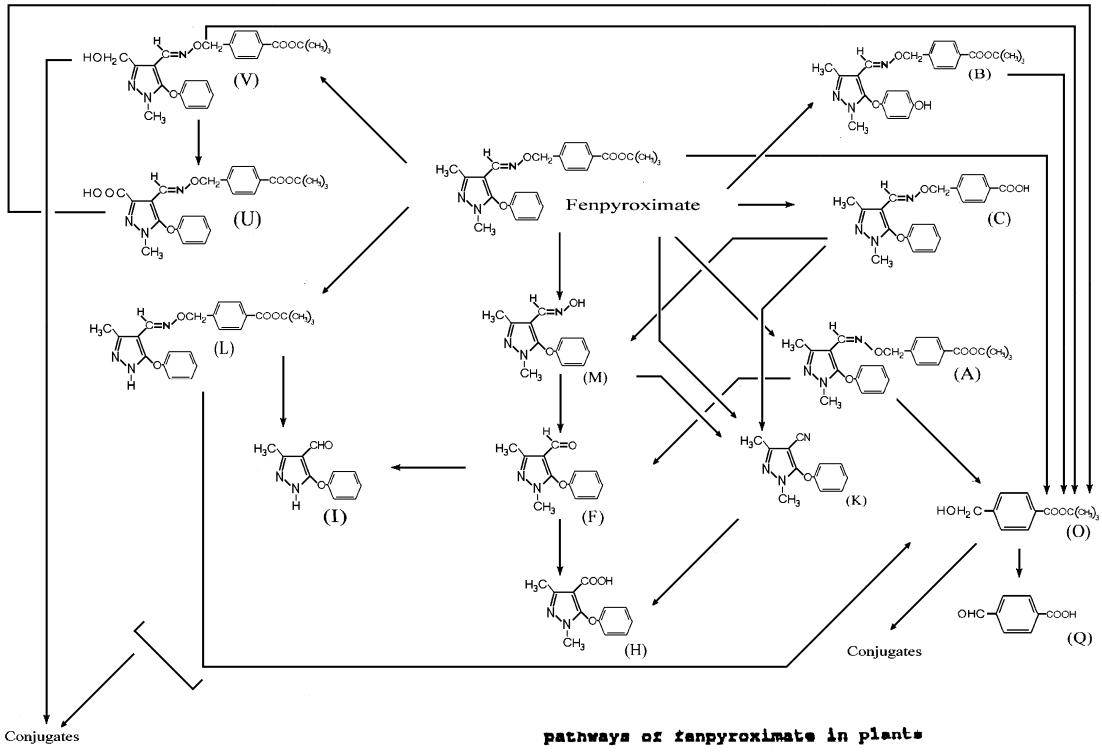
The proposed metabolic pathways of fenpyroximate in plants are shown in Figure 2.

Environmental fate in soil

The degradation of fenpyroximate was studied in upland soils (25 g diluvial and volcanic ash) under laboratory conditions to determine the fate in the field and environment. Soil samples fortified with pyrazole- and benzyl-labelled fenpyroximate (1.30-2.20 mg/kg) were incubated at 25°C for 112 days in the dark, in bottles with traps for CO_2 and volatile organic material.

The compound was degraded with a half-life of 34.3-49.7 days in diluvial soil and 26.3-35.6 days in volcanic ash soil. Eleven degradation products were identified by thin-layer co-chromatography from the pyrazole label, seven from the benzyl. The major degradation products were C, H and K. The other minor products were identified as A, B, F, I, L, M, P, U and V. The $^{14}CO_2$ liberated during the incubation of [*pyrazole*-^{14}C]fenpyroximate amounted to 17.1% of the applied radioactivity in diluvial soil and 16.8% in volcanic soil. With [*benzyl*-^{14}C]fenpyroximate the $^{14}CO_2$ amounted to 64.6% of the applied radioactivity in diluvial soil and 51.2% in volcanic soil. The structures of the identified degradation products suggest that the degradation pathway of fenpyroximate consists in hydrolysis of the ester, isomerization, cleavage to form the oxime, *N*-demethylation, oxidation of the methyl group at the 3-position on the pyrazole ring, hydroxylation of the phenyl ring, and mineralization to CO_2. The degradation products in both soils were determined by TLC with ARG (autoradiography) and radioassay. At day 112 46-58% of the radioactivity from the pyrazole label and 21.3-41.5% of that from the benzyl label was unextractable; most of it was in the humin, humic acid and fulvic acid fractions (Hirano *et al.*, 1990; Izawa *et al.*, 1993).

Figure 2. Proposed metabolic pathways of fenpyroximate in plants.



Three fresh field soils (clay loam, silt loam and sandy loam, with the characteristics shown in Table 10) were treated with [*pyrazole*-^{14}C]fenpyroximate at a rate of 0.2 mg/kg dry soil, corresponding to the highest recommended application rate (150 g ai/ha), and incubated in the dark for 100 days at 20°C under aerobic conditions. The half-lives of fenpyroximate were 16.9, 10.1 and 21.3 days respectively, and the times for the disappearance of 90% of the initial concentration (DT 90) were 186.4, 111.9 and more than 100 days. The degradation products A, C, F, H and K were identified, and five unknown products were found (Römbke and Möllerfeld, 1992a).

Table 10. Characteristics of soils (Römbke and Möllerfeld, 1992a).

%	Clay loam	Silt loam	Sandy loam
Sand	20.2	11.2	30.6
Silt	49.5	65.7	49.7
Clay	30.3	23.1	19.7
Water capacity	55.9	54.1	52.8
Microbial biomass	67.1 initial 47.0 final	29.6 initial 26.4 final	30.4 initial 15.2 final
pH	6.9	6.3	5.9

Both the quantities of degradation products and their rate of formation were different in the three soils, being for example lower in sandy loam than in clay loam (Römbke and Möllerfeld, 1992a)

Another study was carried out to calculate the half-life (DT 50) and DT 90 values using a single standardized sandy soil treated with unlabelled fenpyroximate at the maximum recommended rate of 150 g ai/ha (0.2 mg ai/kg). Portions of 100 g dry weight were incubated in glass tubes (140 cm x 7.5 cm diameter) at 20°C for 100 days in the dark under aerobic conditions.

Fenpyroximate was determined by HPLC. The DT 50 and DT 90 values, calculated by BBA methods, were 159 and more than 200 days, respectively (Römbke and Brodesser, 1992).

The adsorption/desorption of fenpyroximate loamy sand, sandy loam, clay loam and loam was studied in accordance with OECD Guidelines, using ^{14}C-labelled fenpyroximate.

The four soils were sterilized at 120°C for 60 min, because fenpyroximate is readily degraded by soil micro-organisms. Duplicate samples of the soils were agitated for 16 hours with [^{14}C]fenpyroximate solution in a water bath. The amount of fenpyroximate adsorbed was calculated from the difference between the amount recovered from control solutions with no soil and the amount in the supernatants.

The adsorption coefficients (K_{oc}) were 4.53 x 10^4 in sandy loam, 5.36 x 10^4 in loam, 7.95 x 10^4 in clay loam and 12.4 x 10^4 in loamy sand (Takemoto *et al.*, 1990).

In another study the adsorption/desorption of [*pyrazole*-^{14}C]fenpyroximate was determined on sand, sandy loam, clay loam and loam.

The pH of the four soils was between 7.0 and 7.8; the three loams had organic matter contents ranging from 1.4% to 2.1%, and the sand 0.33%. The soils were sterilized by autoclaving for ninety-minute periods daily for three consecutive days.

The adsorption coefficients in this study ranged between 37,000 and 64,000, showing that fenpyroximate was readily adsorbed by the four soils tested; it was not readily desorbed. Fenpyroximate was immobile in the soils studied.

Degradation of fenpyroximate to A and C was observed in all the soils as well as in control solutions (McCann, 1992).

A laboratory column leaching study was carried out with three different sandy soils (German Standard Soils 2.1, sand; 2.2., loamy sand; and 2.3 sandy loam). The soils were characterized by the relative amount of sand, silt and clay, cation exchange capacity, pH (6.1-6.7), maximum water capacity, percentage of organic carbon, and microbial biomass.

The air-dried soils were packed in glass columns with a height of 35 cm and a diameter of 5 cm, and saturated with water. Fenpyroximate was then added as an SC formulation (5.2%) at the highest recommended field application rate of 150 g ai/ha (0.029 mg/column), and the columns kept at 20 ± 2°C in the dark. A total of 393 ml water, equal to 200 mm rainfall, was added dropwise to the soil columns during a period of 2 days. The leachate was collected and analysed by reversed-phase HPLC with UV detection. The fenpyroximate in the soil column (divided into six sections) was also measured at the end of the watering period. The concentration of fenpyroximate in the leachate of the sand was 0.21 mg/l (0.27% of the applied amount), and below the detection limit of 0.1 mg/l (<0.13%) in the other leachates (Römbke, 1992).

An aged column leaching study was carried out according to BBA Guidelines, using a German Standard loamy sand and a glass column with a height of 35 cm and a diameter of 5 cm. The test substance, [*pyrazole*-^{14}C]fenpyroximate, was added at 0.026 mg/column (= 150 g ai/ha) to the standard soil and incubated for 30 days, at which time fenpyroximate and its degradation products

were determined. Aged soil mixture (100 g) was added to a column filled to a height of 28 cm with the same but untreated soil and the column irrigated with 393 ml water for two days. Fenpyroximate and its degradation products were determined in the leachate.

After collecting the leachate the columns were divided into 5 cm sections which were analysed for fenpyroximate and the main degradation products.

The microbial biomass was measured at the beginning and end of the incubation period. The total radioactivity found in the leachate was 1.7% of the amount applied, too low for the identification of products. The total radioactivity detected in the soil was 111.9% of that applied, distributed as follows.

Depth, cm	Extract, %	Residue, %	Total, %
0-5	106.6	2.0	108.6
5-10	2.4	0.3	2.7
10-15	0.6	0	0.6

No activity was detected below 15 cm (Römbke and Möllerfeld, 1992b).

Approximately 5.1% of the total radioactivity could be attributed to the compounds A (3.5%), C (0.4%), H (0.1%) and K (1.1%). The distribution of identified compounds in the top 10 cm of the soil columns was as follows.

Depth, cm	% of applied ^{14}C found as			
	A	C	H	Fenpyroximate
0-5	2.9	0.5	0.1	103.1
5-10	0.2	0.3	0.1	1.6

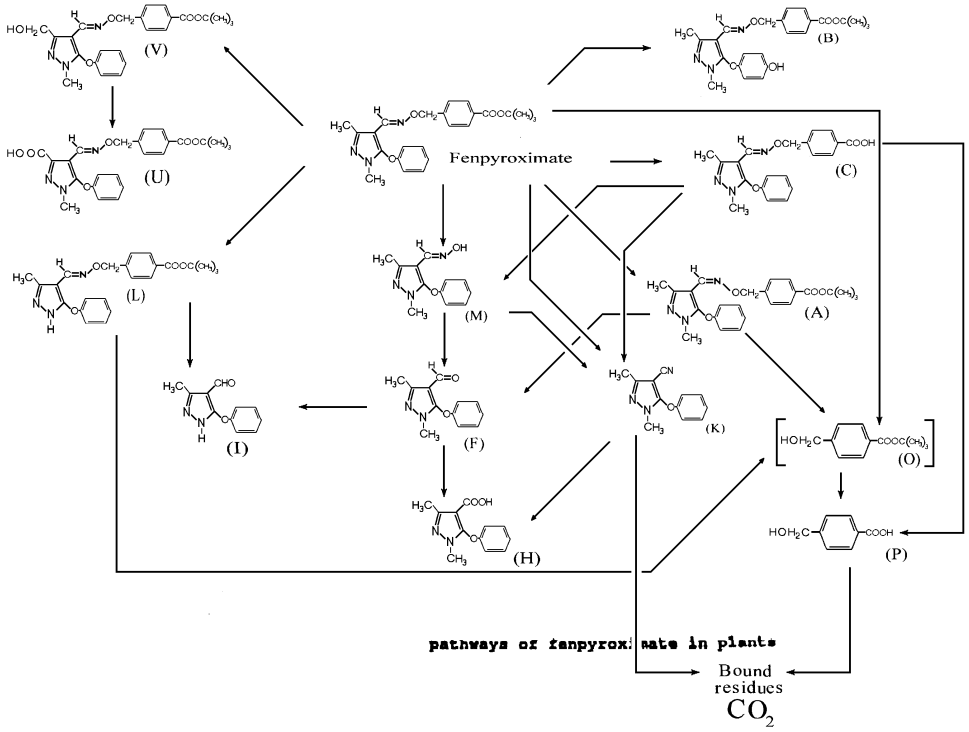
A similar study was carried out with [*benzyl*-^{14}C]fenpyroximate. A small amount of radioactivity was found in the leachate (11%). The major degradation products found after extraction of the soil columns were A and C (Römbke and Möllerfeld, 1992c).

The proposed degradation pathways of fenpyroximate in soil are shown in Figure 3.

Environmental fate in water/sediment systems

In a study of the hydrolysis of fenpyroximate in water according to OECD Guidelines solutions of [*pyrazole*-^{14}C]fenpyroximate (10 ì g/ml) in pH 4.0, 7.0 and 9.0 buffers at 50°C and in pH 7.0 buffer at 40° and 60°C were incubated in the dark. At intervals, the pH 4 and pH 7 solutions were extracted with ethyl acetate, and the pH 9 solution with the same solvent after the addition of 0.5 ml of 1 N HCl.

Figure 3. Degradation pathways of fenpyroximate in soil.



The extracts were analysed by HPLC. The degradation products C and F were identified, C accounting for 60 and 80% of the radioactivity at pH 7.0 and 9.0 after 7 days. The results at 50°C are shown in Table 11 (Nishizawa *et al.*, 1990a).

Table 11. Distribution of radioactivity after incubation of fenpyroximate in buffer solutions at 50°C.

Compound	% of original radioactivity								
	pH 4, at days			pH 7, at days			pH 9, at days		
	1	3	7	1	3	7	1	3	7
Fenpyroximate	82.1	34.3	12.5	88.2	51.3	20.7	74.0	46.0	15.6
C	22.4	39.8	36.8	15.2	29.8	59.8	29.0	46.7	79.2
F	5.4	7.3	34.1	--	--	--	--	--	--

The half-lives of fenpyroximate at 50°C and pH 4.0, 7.0 and 9.0 were 2.28, 3.01 and 2.64 days respectively. The half-life at pH 7 was 10.9 days at 40° and 1.21 days at 60° (Table 12), and was estimated to be 65.7 days at 25° by extrapolation (Nishizawa *et al.*, 1990a).

Table 12. Concentrations of fenpyroximate and compound C in buffer solutions at pH 7 at 40° and 60°C.

Time (days)	% of original radioactivity			
	40°C		60°C	
	Fenpyroximate	Compound C	Fenpyroximate	Compound C
0.5			77.9	23.8
1			57.4	37.8
3	84.7	22.8	18.2	78.7
7	57.3	42.4		
14	39.6	59.6		
21	25.2	53.3		

The hydrolysis of [*pyrazole*-^{14}C]fenpyroximate was studied in sterile aqueous solutions buffered at pH 5, 7 and 9 for 30 days. The solutions were fortified at 9.5 ì g/ml and maintained in a dark chamber at 25 ± 1°C. Duplicate samples were collected after 0, 1, 2, 4, 7, 14, 21 and 30 days, and analysed by HPLC. The samples remained sterile over the course of the study and the pH did not change appreciably.

The half-lives of fenpyroximate were calculated to be 180 days at pH 5, 226 days at pH 7 and 221 days at pH 9. The degradation products A and C were identified at pH 5 and 9, and C also at pH 7 (Saxena and McCann, 1992).

A study of photolysis was carried out to predict the effects of photodegradation in the environment. When fenpyroximate was exposed to sunlight (8 h daily) in a 10 ì g/ml aqueous solution it decomposed with a half-life of 2.6 days and was reduced to 1.7 ì g/ml by the 7th day. Compound A was recognized as a main product at 5.7 and 6.5 ì g/kg at 3 and 7 days respectively (Table 13).

Table 13. Effect of sunlight (8 h/day) on fenpyroximate in water.

Compounds	Concentration, ì g/ml				
	Light, days			Dark, days	
Days	0	3	7	3	7
Fenpyroximate	9.5	4.3	1.7	9.8	9.5
A	<0.5	5.7	6.5	<0.5	<0.5

In an extension of this study aqueous solutions buffered at pH 7 containing pyrazole-, benzyl- or phenyl-labelled fenpyroximate (10 mg/l) were irradiated with a xenon lamp (160,000 lux hr/cm^2) at 25°C for 0, 1, 3 or 6 h. After irradiation, samples were extracted with ethyl acetate, radioactivity was measured by LSC, and products were identified by TLC. The half-life of fenpyroximate was calculated from a decay curve.

Table 14. Photodegradation of [^{14}C]fenpyroximate in water under irradiation with a xenon lamp.

Compound	Radioactivity, % of original										
	[Pyrazole-^{14}C], hours				[Benzyl-^{14}C], hours				[Phenyl-^{14}C], hours		
	0	1	3	6	0	1	3	6	0	3	6
Fenpyroximate	95.1	62.8	46.8	30.0	92.6	75.7	47.4	27.1	96.4	50.7	37
A	0.8	20.4	41.5	47.5	0.7	14.7	41.8	58.3	1.2	41.3	54.3
C + D	2.6	1.8	1.6	1.7	2.5	2.4	1.4	1.9	3.2	1.1	1.4
F	<0.2	0.6	2.2	2.9	--	--	--	--	<0.2	3.5	6.6
M	<0.2	0.2	0.8	0.6	--	--	--	--	<0.2	0.2	<0.2
O	--	--	--	--	<0.2	<0.2	0.5	1.0	--	--	--
Others	0.2	2.9	0.9	2.5	<0.2	<0.2	2.5	5.6	<0.2	1.1	1.7
Half-life of fenpyroximate, h			2.9				2.8			3.1	

Half-lives from 2.8 to 3.1 hours were calculated for the three labelled compounds, and A was again the main product. The addition of acetone (2%), a photo-sensitizer, accelerated the degradation of fenpyroximate. Compounds F, K, M and O, in addition to A, were identified as photodegradation products (Nishizawa *et al.*, 1990b).

An additional study, according to EPA guidelines, investigated the photodegradation of [*pyrazole*-^{14}C]fenpyroximate in 0.01 M phosphate buffer solution (10 mg/l) at pH 7.0. The study was in two parts: (1) to determine the first order rate constant and half-life of fenpyroximate, and (2) to determine the half-life of A, its geometric isomer.

In part 1, duplicate samples were collected after 0.5, 1, 2, 3, and 4 hours of continuous irradiation with a xenon lamp (603 watts, 290-300 nm) to estimate the half-life of fenpyroximate. In part 2 the samples were collected after 4, 12, 24, 48 and 73 hours of continuous irradiation to generate the isomer A and estimate its half-life. Samples were extracted with ethyl acetate and analysed by HPLC.

The half-life of fenpyroximate was estimated to be 1.5 hours, and that of A 10.5 hours. Only one other degradation product (K) accounted for more than 10% of the original radioactivity. Volatile radioactivity accounted for less than 1% of that originally present (Swanson, 1993).

The proposed degradation pathways of fenpyroximate in water are shown in Figure 4.

Figure 4. Degradation of fenpyroximate in water

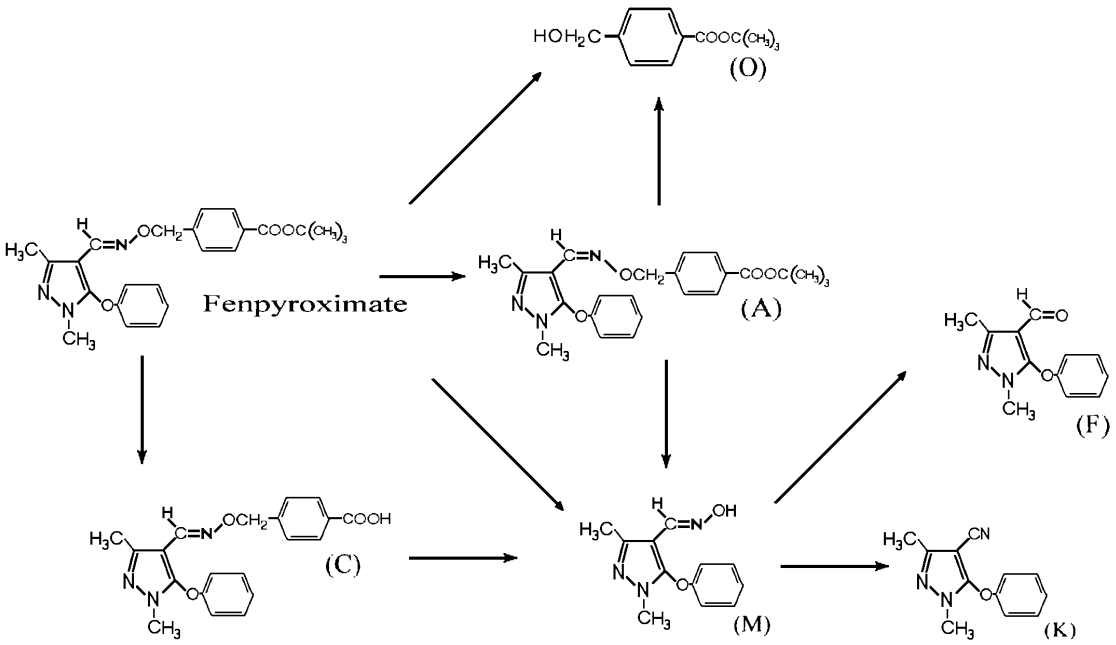


Figure 5. Proposed metabolic pathways of fenpyroximate in water

METHODS OF RESIDUE ANALYSIS

Analytical methods

The following methods were used to determine residues in supervised trials.

Fruits, vegetables and tea. The homogenized sample is extracted with methanol and filtered by suction through Celite. After concentration in a rotary evaporator, the extract is partitioned with n-hexane and acetonitrile and cleaned up on a silica gel/alumina column, eluting with n-hexane/ethyl acetate. After evaporation of the eluant, the residue is redissolved in 1,4-dioxane and analysed by GLC with an NPD. Fenpyroximate and its *Z*- isomer (A) are determined in the same extract (Nihon Nohyaku, 1989a). The reported recoveries and limits of detection are shown Table 15.

Table 15. Recoveries and limits of detection of fenpyroximate and its *Z*- isomer.

Sample	Added, mg/kg	Recovery, %		Limit of detection
		Fenpyroximate	*Z*- isomer	
Orange peel	0.2	93	87	0.02
Orange pulp	0.1	92	81	0.01
Apple	0.1	105	88	0.01
Strawberry	0.1	91	78	0.01
Tea	0.2	78	85	0.02

The parent compound, its *Z*- isomer and demethyl-fenpyroximate can be determined in the same extract by HPLC using an ultraviolet photometric detector. Homogenized samples are extracted with acetonitrile, partitioned in hexane/water and cleaned up on a silica gel/alumina column, using n-hexane/ethyl acetate (7:3) as eluant. The residue, dissolved in acetonitrile/water (3:2), is cleaned up on C_{18} and silica cartridges, again eluting with n-hexane/ethyl acetate. The eluant is evaporated and the residue dissolved in acetonitrile for HPLC analysis on a 4 x 250 mm RP-18 column, with detection at 258 nm. The L0D is 0.02 mg/kg. Recoveries are shown in Table 16 (Nihon Nohyaku, 1989b).

Table 16. Recoveries of fenpyroximate, its *Z*- isomer and demethyl-fenpyroximate from mandarin orange pulp and grapes.

Sample	Added, mg/kg	Recovery %		
		Fenpyroximate	*Z*- isomer	Demethyl-fenpyroximate
Orange pulp	0.1	96	98	88
Grapes	0.1	103	90	78

In another method GLC with an NPD is used to determine fenpyroximate and its *Z*- isomer, and HPLC with an ultraviolet detector to determine demethyl-fenpyroximate. The homogenized sample is extracted with acetonitrile and the extract cleaned up by solid-phase chromatography on a silica gel/alumina column, silica cartridge and/or C_{18} cartridge. The reported recoveries were 99% for the GLC determination and 80% (from green peppers) for the HPLC. The reported limit of detection by both methods was 0.01 mg/kg (Nihon Nohyaku, 1989c).

The analytical methods of the Deutsche Forshungsgemeinschaft were adapted for the residue determination of fenpyroximate and its *Z*- isomer in orange pulp and peel, apple fruit, mash and cider and grapes and wine, and the processing products of hops (dregs, yeast and beer) (Specht, 1992a-d).

Homogenized samples are extracted with acetone, after the addition of sufficient water to bring the acetone: water ratio to 2:1 v/v. The extract is saturated with sodium chloride and partitioned with dichloromethane. Beer is simply diluted with sodium chloride solution and extracted with dichloromethane. The solvent is evaporated and the residue cleaned up by automated gel-permeation chromatography on Bio Beads S-X3 polystyrene gel, using a mixture of cyclohexane and ethyl acetate (1 + 1) as eluant. The fraction containing the residue is concentrated and, after supplemental clean-up on a small silica gel column, analysed by GLC using a wide-bore capillary column and nitrogen-sensitive alkali flame ionization detector. The limits of determination of both compounds were 0.05 mg/kg for grapes, wine, orange pulp and peel, and apple fruit, mash and cider; 0.1 mg/kg for dregs and yeast from hops, and 0.01 mg/kg for beer.

Recoveries of fenpyroximate and the isomer were in the range 74 to 100% from orange pulp and peel at fortification levels of 0.05, 0.5 and 5.0 mg/kg (Specht, 1992a), from grapes and wine at 0.05 and 0.5 mg/kg and from grapes at 2.0 mg/kg (Specht, 1992c). Recoveries from apple fruit, mash and cider at 0.05 and 0.5 mg/kg and from fruit at 5 mg/kg ranged from 70 to 100% (Specht, 1992b). Recoveries from beer at 0.01 and 0.10 mg/l and from dregs and yeast at 0.1 and 1.0 mg/kg ranged from 79% to 115% (Specht, 1992d). All the studies were carried out in compliance with GLP.

A simplified HPLC method was used for residue analysis in several supervised trials. Samples were extracted with acetonitrile and concentrated. The concentrate was cleaned up on a C_{18} cartridge eluted with methanol, then on a silica gel cartridge eluted with diethyl ether/n-hexane. HPLC was on an RP-18 column with a UV detector (wavelength 258 nm). The LOD was 0.005 mg/kg. Recoveries at 0.2 mg/kg fortification levels from citrus pulp and peel and 0.2-0.5 mg/kg from apples were reported to be over 90% for fenpyroximate, its *Z*- isomer and demethyl-fenpyroximate (Iawamoto and Matano, 1993a,b).

Soil. The parent compound and its degradation products A, C, H and K are easily extractable from soil. Samples are extracted with a mixture of acetonitrile and 1M aqueous ammonium chloride (4:1). The extract is cleaned up by partition of an acidic aqueous solution (1M HCl) with dichloromethane, followed by column chromatography on silica gel/alumina and Florisil. The carboxyl groups of C and H are methylated with diazomethane before column chromatography. The residues are determined in a single aliquot by gas chromatography with an NPD. Recoveries at fortification levels of 25 and 250 ì g/kg ranged from 90 to 100% for fenpyroximate and from 72 to 100% for the other compounds (Nishizawa *et al.*, 1992).

Water. For the analysis of water for fenpyroximate and its *Z*- isomer samples are extracted with n-hexane, cleaned up on a silica gel cartridge, and determined by HPLC with UV detection. The recoveries from river water, well water and distilled water were 82-87% for fenpyroximate and 78-85% for the isomer at 5 ì g/l. The reported limit of detection was 0.1 ì g/l for both compounds (Funayama *et al*., 1991).

Stability of pesticide residues in stored analytical samples

Fenpyroximate and its degradation products were added to soil at 250 ì g/kg, and samples stored at -20°C for 120 days were analysed in duplicate. The results were 86-88% of the initial values for fenpyroximate, and 90-116% for the other compounds.

The stability of pyrazole-labelled fenpyroximate was studied in apples and grapes stored at about -20°C for approximately three years. The studies were reported to be in compliance with GLP.

Apples were treated with [*pyrazole*-^{14}C]fenpyroximate, harvested at maturity 57 days after treatment, and then analysed. After 3 years frozen storage, apples of the same batch were analysed by the same procedure. The nature and relative levels of the metabolites remained unchanged. The variation in the residues (Table 17) was attributed to inhomogeneity of the sub-samples (Wyss-Benz, 1993a).

Bunches of grapes from vines treated 57 days previously were analysed. Replicate samples were analysed after storage at about -20° for 3 years (Wyss-Benz, 1993b). The results are shown in Table 17.

Table 17. Total ^{14}C residues before and after frozen storage (Wyss-Benz, 1993a,b).

Sample	Residue[1] October 1990	Residue[1] September 1993
Apples	0.031	0.020
Grapes	0.070	0.045

[1] Total ^{14}C expressed as mg fenpyroximate/kg fresh wt

In a storage stability study on apples fortified with fenpyroximate, the *Z*- isomer and demethyl-fenpyroximate, homogenized samples were stored at -20°C until analysis after 18 and 145 days. The remaining levels of fenpyroximate, *Z*- isomer and demethyl compound were 68.0-68.1, 71.0-72.2 and 57.2-66.3% of the initial values respectively (Iawamoto and Matano, 1993b).

Grapes fortified with fenpyroximate, the *Z*- isomer and *N*-demethyl-fenpyroximate were stored at -20°C. Fenpyroximate and the *Z*- isomer were determined after storage for 77 days and *N*-demethyl-fenpyroximate after 119 days. The mean remaining levels of the three compounds were 76.1, 87.6 and 49.7% of the initial values respectively (Iawamoto and Matano, 1993e,d).

A study to determine the effect of storage at -18°C on the residues of fenpyroximate and the *Z*- isomer in dried hop cones was carried out using the analytical method DFG S 19. Untreated and fortified samples were analysed in duplicate. Samples were spiked to obtain a level of 9.6 mg/kg fenpyroximate and 9.68 mg/kg of the *Z*- isomer.

No significant decrease of fenpyroximate, the isomer or their sum was observed during a storage period of 24 months (Weber, 1994).

Table 18. Stability of residues in stored hop samples (dried cones).

Compound	% of initial residue, storage time (months)					
	1 day	3	6	12	18	24
Fenpyroximate	97	85	97	88	91	109
Z- isomer (A)	75	89	78	60	90	66
Sum of A and fenpyroximate	104	107	95	105	108	105

The stability of fenpyroximate was also studied in stored citrus samples. Pulp samples fortified with fenpyroximate and the *Z*- isomer (0.4 mg/kg and 0.079 mg/kg respectively) and stored at -20°C for 140 days contained 65 and 62% of the initial level respectively. In peel, fenpyroximate and the *Z*- isomer were added at 1.0 and 0.195 mg/kg respectively: after storage at -20°C for 188 days 73 and 72% of these levels remained respectively (Iawamoto and Matano, 1993a).

Residue definition

Fenpyroximate is the major component of the residues remaining in crop commodities. The *Z*- isomer (compound A) and *N*-demethyl-fenpyroximate (compound L) were the only metabolites found at analytically significant levels, and only in mandarin peel. Compound L was not detected in any other commodities and compound A was at levels near or below the limit of determination. The residue should therefore be defined as fenpyroximate.

USE PATTERN

Fenpyroximate is a non-systemic miticide for the control of immature and adult stages. It is registered in several countries, principally for the control of the European red mite (*Panonychus ulmi*) and the two-spotted mite (*Tetranichus urticae*), on pome fruits, citrus, grapes and hops. It is applied as a foliar spray. It is available as a 5% suspension concentrate. Registered uses are listed in Table 19.

Table 19. Registered uses of fenpyroximate on fruit and hops. All formulations are 5% SC. All applications are foliar.

Crop	Country	Application			PHI, days
		Kg ai/ha	Spray conc., kg ai/hl	No.	
Citrus	Brazil	0.15	0.005	1	15
	Chile	-	0.0025	1	14
	Greece	0.12-0.16	0.004-0.005	1	14
	Italy	0.1	0.005	1	14
	Japan		0.003-0.005	1	14
	Peru		0.005	-	-
	Spain	0.2	0.005	1	14
Pome fruits	Argentina		0.0025-0.0037	1	14
	Chile		0.0025	1	21
	Malaysia	0.01-0.02	0.005	1	7
	New Zealand	0.05-0.075	0.0025	1	14
	Peru		0.005		
	Portugal	0.05-0.075	0.005-0.0075	1	14
	Spain	0.11	0.008	1	7
Apple	Brazil	0.06	0.005	1	15
	France	0.06-0.08	0.008	1	21
	Germany	0.112	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
	Portugal	0.05-0.08	0.005-0.008	1	28
	Switzerland	0.1-0.15	0.005-0.008	1	21
	UK	0.1	-	1	14
Grapes	Chile		0.0025	1	30

Crop	Country	Application			PHI, days
		Kg ai/ha	Spray conc., kg ai/hl	No.	
	Germany	0.105-0.120	0.0075	1	35
	Italy	0.05		1	14
	Japan		0.003-0.005	1	14
	Peru		0.005	-	-
	Portugal	0.05-0.08		1	14
	Spain	0.04		1	14
	Switzerland	0.1-0.15	0.005-0.008	1	21
Hops	Germany	0.225-0.263	0.0075	1	21
	Italy	0.05		1	14
	Japan		0.005	1	14

RESIDUES RESULTING FROM SUPERVISED TRIALS

Residue data were provided from trials on citrus fruits, apples, grapes and hops. In many of the trials the *Z*- isomer was also determined. Results are shown in Tables 20-23, in which residues from treatments according to GAP are underlined.

Citrus fruit (Table 20). Fenpyroximate 5% SC is registered for use on citrus fruits in several countries. One application is recommended at rates of 0.1-0.2 kg ai/ha and PHIs of 14 or 15 days.

A summary report of six supervised trials carried out on mandarins in Italy in 1991 was provided. Three trials were with one application at the recommended rate (0.1 kg ai/ha) and the other three were at a double rate. Residues were determined in the pulp and peel. No data were available on whole fruit.

Another study was carried out on satsuma mandarins growing in a greenhouse with fenpyroximate 5% SC applied at the GAP concentration of 0.005 kg ai/hl in Japan. Residues of fenpyroximate 14 or more days after application in whole fruit, pulp and peel were 0.019-0.21, <0.005-0.027 and 0.068-0.98 mg/kg respectively. Residues in the whole fruit were estimated from the weight ratio of pulp to peel.

Samples were analysed by HPLC 130 days after sampling. Recoveries were determined by fortification of control samples with fenpyroximate, the *Z*- isomer and *N*-demethyl-fenpyroximate. Mean recoveries were fenpyroximate 98% (pulp and peel), *Z*- isomer 76% (pulp and peel) and *N*-demethyl fenpyroximate 78% (peel) and 100% (pulp) (Iawamoto and Matano, 1993a).

Oranges, Sweet. Summary data on supervised trials were provided from Brazil, Greece and Italy. Four supervised field trials were carried out in Brazil with 2 applications between 0.08 and 0.36 kg ai/ha. Samples were analysed by HPLC with an LOD of 0.05 mg/kg. Recoveries were 77-87% for fenpyroximate and 87-89% for the *Z*- isomer. In the trials in Greece and Italy analyses were by the DFG S 19 method: residues in the whole fruit were not determined.

Table 20. Residues of fenpyroximate and its *Z*- isomer in citrus treated with fenpyroximate 5% SC.

Country, year, crop	Application	PHI, days	Fenpyroximate	*Z*- isomer	Ref.

	kg ai/ha	kg ai/hl	No		Pulp	Peel	Whole fruit	Pulp	Peel	
Brazil (1989-1990) Oranges	0.08	0.005	2	15	<0.05	0.2		<0.05	0.05	R.08
				30	<0.05	<0.05		<0.05	<0.05	
	0.16	0.01	2	15	<0.05	0.1		<0.05	0.06	R.09
				30	<0.05	<0.05		<0.05	<0.05	
	0.18	0.005	2	16	<0.05	0.38		<0.05	0.08	R.10
				29	<0.05	0.18		<0.05	0.05	
	0.36	0.01		16	0.08	0.73 0.85		<0.05	0.21 (2)	R.11
				29	<0.05	0.59		<0.05	0.13	
Greece 1992 Oranges	0.15	0.005	1	0	<0.01	0.35		<0.01	<0.01	R.12
				2	<0.01	0.37		<0.01	<0.01	
				9	<0.01	0.3		<0.01	<0.01	
				16	<0.01	0.26		<0.01	<0.01	
				22	<0.01	0.13		<0.01	<0.01	
				28	<0.01	0.18		<0.01	<0.01	
	0.31	0.01	1	0	<0.01	0.31		<0.01	<0.01	R.13
				2	<0.01	0.28		<0.01	<0.01	
				9	<0.01	0.19		<0.01	<0.01	
				16	<0.01	0.24		<0.01	<0.01	
				22	<0.01	0.19		<0.01	<0.01	
				28	<0.01	0.23		<0.01	<0.01	
Italy 1990 Oranges	0.077	0.0075	2	21	0.05	0.38		<0.05	<0.05	R.14
				64	<0.05	0.39		<0.05	<0.05	
				113	<0.05	0.35		<0.05	<0.05	
	0.077	0.0075	2	21	<0.05	0.3		<0.05	<0.05	R.15
				63	<0.05	0.26		<0.05	<0.05	
				105	<0.05	0.36		<0.05	<0.05	
	0.077	0.0075	2	21	0.06	0.54		<0.05	<0.05	
				63	<0.05	0.53		<0.05	<0.05	R-16
				84	<0.05	0.4		<0.05	<0.05	
	0.15	0.015	2	21	0.08	0.73		<0.05	<0.05	
				64	<0.05	0.77		<0.05	<0.05	R-17
				113	<0.05	0.62		<0.05	<0.05	
	0.15	0.015	2	21	<0.05	0.96		<0.05	<0.05	
				63	<0.05	0.57		<0.05	<0.05	R-18
				105	<0.05	0.71		<0.05	<0.05	
				21	0.08	0.83		<0.05	<0.05	
				63	<0.05	0.75		<0.05	<0.05	R-19
				84	<0.05	0.72		<0.05	<0.05	
Italy 1991 Mandarins	0.10	0.006	1	28	0.01	0.35		<0.01	<0.01	R-01

Country, year, crop	Application			PHI, days	Fenpyroximate			*Z*- isomer		Ref.
	kg ai/ha	kg ai/hl	No		Pulp	Peel	Whole fruit	Pulp	Peel	
					<0.01	0.42		<0.01	0.02	R-03
	0.20	0.013	1	28	0.03 0.03	0.78 0.86		<0.01 <0.01	<0.01 0.03	R-02 R-04
	0.10	0.006	1	0	0.03	0.52		<0.01	0.02	R-05
				5	0.02	0.5		<0.01	0.02	
				10	<0.01	0.36		<0.01	<0.01	
				14	<0.01	0.34		<0.01	<0.01	
				25	0.02	0.24		<0.01	<0.01	
				28	<0.01	0.13		<0.01	0.01	
	0.20	0.013	1	0	0.05	0.45		<0.01	<0.01	
				5	0.06	0.63		<0.01	<0.01	R-06
				10	0.03	0.57		<0.01	0.04	
				14	0.03	0.83		<0.01	0.03	
				21	0.02	0.59		<0.01	0.03	
				28	0.01	0.59		<0.01	0.03	
Japan 1989 Mandarins, Greenhouse	0.25	0.005	1	7	0.006 0.006	0.15 0.14	0.028	<0.005 (2)	<0.005 (2)	R-07
				14	<0.005 (2)	0.15 0.14	0.026	<0.005 (2)	<0.005 (2)	
				21	0.009 (2)	0.08 0.068	0.019	<0.005 (2)	<0.005 (2)	
				30	0.008 0.007	0.17 (2)	0.037	0.005 (2)	0.008 0.007	
				44	0.007 (2)	0.21 0.18	0.04	<0.005 (2)	0.007 0.008	
	0.5	0.005	1	7	0.027 0.024	0.99 0.96	0.20	<0.005 (2)	0.024 0.022	
				14	0.023 0.019	0.98 0.97	0.21	<0.005 (2)	0.045 0.043	
				21	0.01 0.01	0.69 0.66	0.15	<0.005 (2)	0.035 0.033	
				30	0.01 0.01	0.67 0.65	0.12	<0.005 (2)	0.04 (2)	
				44	<0.005 (2)	0.72 0.68	0.13	<0.005 (2)	0.044 0.042	

Apples (Table 21). Supervised trials were carried out in Australia to determine residues of fenpyroximate, its *Z*- isomer and the demethyl metabolite in apples following the application of fenpyroximate approximately 4 weeks before harvest at rates of 0.083 and 0.16 kg ai/ha. Information on GAP in Australia was not provided. The metabolites were not detected at the limit of determination of 0.01 mg/kg (Bull and Holding, 1992).

In Belgium, two supervised trials were carried out to establish a decary curve and to determine fenpyroximate and its isomer in apples. No information on GAP was provided. No residues of the metabolite were found above the limit of determination of the method (0.02 mg/kg). Residues of

fenpyroximate were 0.10 and 0.08 mg/kg after 14 and 21 days from treatment at 0.090 kg ai/ha, close to the French GAP rate (Benet and Deerecke, 1992).

Nine trials were carried out on apples in France at rates of 0.06, 0.08, 0.17 and 0.24 kg ai/ha. Samples were analysed according to GLP, by a modified HPLC method. No residues of the two metabolites were found above the limit of determination (0.02 mg/kg), except a residue of 0.03 mg/kg of the *Z*- isomer after treatment at the highest rate. Residues of fenpyroximate from treatment according to GAP (single applications of 0.06-0.08 kg ai/ha) were 0.02-0.09 mg/kg at the GAP PHI of 21 days (Benet and Masserot, 1991).

Eleven supervised trials were carried out in Germany (1989-90) on four varieties (Golden Delicious, James Grieve, Gloucester and Jonathan) at different locations. The application rates were 0.064-0.15 kg ai/ha. Residues of fenpyroximate 21 days after the last application approximating the GAP rate of 0.112 kg ai/ha were <0.05-0.24 mg/kg. Residues of the *Z*- isomer were all below 0.05 mg/kg (Burstell *et al*., 1991a,b,1992a).

Two supervised field trials were carried out in Japan, with single applications at 0.005 kg ai/hl, in accordance with GAP. Residues of fenpyroximate 15 days after application were 0.05 and 0.11 mg/kg. Residues of the *Z*- isomer were <0.005 and 0.006 mg/kg.

In New Zealand, 14 trials were carried out from 1991 to 1994. Apple trees were treated with fenpyroximate as recommended, one application at 0.0025 kg ai/hl, and at a double concentration. Residues of fenpyroximate in samples treated at the GAP concentration were <0.01-0.13 mg/kg after the registered PHI of 14 days. Metabolites were not determined.

Table 21. Residues of fenpyroximate and its isomer in apples treated with fenpyroximate 5% SC

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
Australia 1992	0.083	0.005	1	0	0.09, 0.07, 0.1, 0.13	<0.01 (4)	R-20
				7	0.08, 0.10, 0.05, 0.06	<0.01 (4)	
				14	0.14, 0.12, 0.08, 0.18	<0.01 (4)	
				24	0.06 (2), 0.03, 0.17	<0.01 (4)	
	0.16	0.01	1	0	0.34, 0.30, 0.23 (2)	<0.01 (4)	
				7	0.19, 0.33, 0.29, 0.22	<0.01 (4)	
				14	0.19 (2), 0.18, 0.17	<0.01 (4)	
				24	0.12, 0.19, 0.08 (2)	<0.01 (4)	
Belgium 1991	0.090	0.006	1	7	0.12	<0.02	R-21
				14	0.10	<0.02	
				21	0.08		
				28	0.05		
	0.18	0.012	1	7	0.19	<0.02	
				14	0.17	<0.02	
				21	0.14		
				28	0.18		
France 1989	0.06	0.006	1	0	0.1	<0.02	R-22
				7	0.08		
				14	0.03		

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
				21	0.02		
				29	0.03		
	0.06		2	48	0.05	<0.02	
				53	0.07		
				69	0.03		
	0.08	0.008	2	48	0.08	<0.02	
				53	0.03		
				69	0.04		
France 1990	0.08	0.008	1	0	0.11, 0.12	<0.02 (2)	R-22
				7	0.05, 0.08	<0.02 (2)	
				14	0.06, 0.10	<0.02 (2)	
				20-21	0.05, 0.09	<0.02 (2)	
				29	0.03, 0.06	<0.02 (2)	
	0.06	0.006	2	24	0.11	<0.02	
				68	0.05	<0.02	
	0.08	0.008	2	24	0.16	<0.02	
				68	0.07	<0.02	
	0.17	0.006	2	45	0.08	<0.02	
	0.23-0.24	0.008	2	45	0.19	0.03	
France 1991	0.08	0.008	1	30	0.03		R-23
				50	0.03		
				75	<0.02		
				106	<0.02		
				120	<0.02		
				144	<0.02		
Germany 1989	0.1125	0.0075	2	0	0.1, 0.19	<0.01, 0.01	R-24
				7	0.12, 0.18	<0.01, 0.01	
				14	0.11, 0.1	<0.01, 0.01	
				21	0.1, 0.09	<0.01 (2)	
	0.0643-0.0868	0.0075-0.0073	2	0	0.12	<0.01	
				7	0.12	0.01	
				14	0.08	0.01	
				21	0.09, 0.12	0.01	
	0.1- 0.115	0.0075-0.0076	2	0	0.21	<0.01	
				7	0.19	0.01	
				14	0.15	0.01	
				21	0.16	0.01	
	0.15	0.001	2	0	0.23, 0.24	0.02	R-25
				7	0.23	0.01	
				14	0.24	0.02	
				21	0.24	0.02	

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
	0.095, 0.132	0.01	2	0	0.12	<0.01	
				7	<0.01 (2)	<0.01	
				14	0.12	0.01	
				21	0.12	0.01	
Germany 1990	0.064	0.0075	1	0	0.15	<0.05	R-26
				7	0.11	<0.05	
				14	0.16	<0.05	
				28	0.12	<0.05	
				42	0.09	<0.05	
				56	0.06	<0.05	
				70	<0.05	<0.05	
				81	<0.05	<0.05	
				92	<0.05	<0.05	
	0.1125	0.0075	1	0	0.13	<0.05	R-26
				7	0.14	<0.05	
				14	0.11	<0.05	
				28	0.08	<0.05	
				42	0.06	<0.05	
				56	<0.05	<0.05	
				70	<0.05	<0.05	
				84	<0.05	<0.05	
				91	<0.05	<0.05	
	0.075	0.0075	2	0	0.13	<0.05	R-27
				7	0.08	<0.05	
				14	0.08	<0.05	
				21	0.06	<0.05	
				28	<0.05	<0.05	
	0.081	0.0075	2	0	0.24	<0.05	
				7	0.21	<0.05	
				14	0.18	<0.05	
				21	0.15	<0.05	
				28	0.13	<0.05	
	0.1125	0.0075	2	0	0.21	<0.05	
				7	0.17	<0.05	
				14	0.13	<0.05	
				21	0.08	<0.05	
				28	0.11	<0.05	
	0.114	0.0076	2	0	0.05	<0.05	
				7	<0.05	<0.05	
				14	<0.05	<0.05	
				21	<0.05	<0.05	

Country, Year	Application			PHI, days	Residues mg/kg		Ref.
	kg ai/ha	kg ai/hl	No		Fenpyroximate	Z- isomer	
				28	<0.05	<0.05	
Japan 1990	0.14	0.005	1	15	0.11	0.006	R-28
				30	0.08	0.005	
				45	0.034	<0.005	
				60	0.042	<0.005	
	0.25	0.005	1	15	0.048	<0.005	
				30	0.028	<0.005	
				45	0.007	<0.005	
				60	<0.005	<0.005	
New Zealand 1991/92		0.0025 (3 trials)	1	7-9	0.07, 0.09, 0.12		R-29
				14	0.12, 0.13, 0.03		
				28	<0.01 (3)		
				42-43	<0.01 (2), 0.01		
		0.005 (3 trials)	1	7-9	0.1, 0.07, 0.06		
				14	0.05, 0.04, 0.02		
				21	<0.01		
				28	0.03 (2), <0.01		
				42-43	<0.01 (2), 0.01		
				52-56	<0.01 (3),		
New Zealand 1993/94		0.0025 (4 trials)	1	7-9	0.05, 0.06, 0.01 (2)		R-30
				14	0.03 (2), <0.01, 0.04		
				21	0.04 (2), 0.02, <0.01		
				28	0.03, 0.02, <0.01 (2)		
				35	0.02 (2), 0.01,<0.01		
				42-43	0.02 (3), <0.01		
				49	0.02, 0.01, <0.01		
				52-56	0.01, <0.01 (2)		
		0.005 (4 trials)	1	7-9	0.11, 0.07, 0.06, 0.05		
				14	0.08, 0.06 (2), 0.03		
				21	0.03, 0.04, 0.05, 0.06		
				28	0.03 (2), 0.05, 0.02		
				35	0.03 (2), 0.04, 0.01		
				42-43	0.04, 0.03 (2), <0.01		
				49	0.03, 0.02, 0.01		
				52-56	0.03, 0.01, <0.01		

Grapes (Table 22). Fenpyroximate 5% SC is registered for use on vines in Chile, Peru, Japan and

several European countries.

In France, six supervised trials (two designed to establish decay curves) were carried out on vines in 1989 and 1990. Grapes and wine were analysed for fenpyroximate and its two major metabolites. For the dissipation studies, fenpyroximate was applied at rates of 0.06 kg ai/ha in 1989 and 0.08 kg ai/ha in 1990. Residues of fenpyroximate in grapes decreased from 0.1 to 0.07 mg/kg in 30 days when the vines were treated at 0.08 kg ai/ha. After treatment at 0.06 kg/ha all residues after 7 days and later were <0.02 mg/kg. The other trials were with two applications of 0.06 or 0.08 kg ai/ha and harvest was after 36 to 55 days. Residues of fenpyroximate in the grapes ranged between <0.02 and 0.14 mg/kg. Residues of the metabolites were <0.02 mg/kg. There was no information on GAP in France.

Eight supervised field trials were carried out at different locations in Germany. Grapes were analysed for fenpyroximate and its *Z*- isomer. The last treatment was at the beginning of ripening and sampling was at intervals up to 35 days (maturity). The vines were treated twice at 0.14 or 0.18 kg ai/ha, or once at 0.045 kg ai/ha and again at 0.135 kg/ha. Residues of fenpyroximate and the metabolite after 35 days were 0.06-0.4 mg/kg and ≤0.01 mg/kg respectively.

Six trials were carried out in Italy on wine grapes at application rates of 0.064-0.19 kg ai/ha. The GAP rate is 0.05 kg ai/ha. Grapes samples were taken at the GAP PHI of 14 days. Residues of fenpyroximate and its isomer were 0.07-0.57 mg/kg and <0.01 mg/kg respectively.

In residue trials in Japan (1988 and 1989) in greenhouses fenpyroximate was applied once or twice at the GAP concentration of 0.005 kg ai/hl (a single application is GAP). Samples were taken 13, 20 and 29 days after application. Residues of fenpyroximate were 0.06-0.05 mg/kg from single applications and about 1.2 mg/kg from two applications. Residues of the *Z*- isomer were <0.005-0.014 mg/kg (Iwamoto and Matano, 1993c,d).

Table 22. Residues of fenpyroximate and its isomer in grapes from supervised trials.

Country, Year, Location	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
France 1989	0.06	0.006	1	0	0.05	<0.02	R-31
				7	<0.02	<0.02	
				14	<0.02	<0.02	
				21	<0.02	<0.02	
				29	<0.02	<0.02	
		0.006	2	36	0.05	<0.02	
				37	0.07	<0.02	
				47	<0.02	<0.02	
France 1990	0.06	0.006	2	42	0.05	<0.02	
				46	0.07	<0.02	
				55	0.06	<0.02	
France 1990	0.08	0.008	1	0	0.1	<0.02	
				7	0.05	<0.02	
				14	0.05	<0.02	
				21	0.08	<0.02	
				30	0.07	<0.02	

Country, Year, Location	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
France 1989	0.08	0.008	2	36	<0.02	<0.02	
				37	0.14	<0.02	
				47	<0.02	<0.02	
France 1990	0.08	0.008	2	42	0.08	<0.02	
				46	0.05	<0.02	
				55	0.04	<0.02	
Germany 1989 (Mussbach)	0.14	0.023	2	0	0.17	<0.01	R-32
				7	0.12	<0.01	
				14	0.11	<0.01	
				28	0.09	<0.01	
				35	0.06	<0.01	
Germany 1989 (Kappelrodeck)	0.14	0.023	2	0	0.41	<0.01	R-33
				7	0.41	<0.01	
				14	0.27, 0.34	0.01	
				28	0.32	0.01	
				35	0.4	<0.01	
Germany 1989 Pfeddersheim	0.18	0.03	2	0	0.2	<0.01	R-34
				7	0.12, 0.17	<0.01	
				14	0.14	<0.01	
				28	0.21	<0.01	
				35	0.15	<0.01	
Willsbach	0.18	0.03	2	0	0.19 (2)	<0.01	R-35
				7	0.18	<0.01	
				14	0.24	<0.01	
				28	0.16	<0.01	
				35	0.13, 0.14	<0.01	
Germany 1989 Mussbach	0.18	0.03	2	0	0.26	<0.01	R-36
				7	0.16	<0.01	
				14	0.1 (2)	<0.01	
				28	0.13	<0.01	
				35	0.13	<0.01	
Germany 1989 Kappelrodeck	0.18	0.03	2	0	0.29	<0.01	R-37
				7	0.3 (2)	<0.01	
				14	0.18	<0.01	
				28	0.12	<0.01	
				35	0.16	<0.01	
Germany 1991 Nittel	0.045-0.135	0.015-0.225	2	0	0.22	0.02	R-38
				7	0.16	0.02	
				14	0.16	0.02	
				28	0.1	0.01	
				35	0.08	0.01	

Country, Year, Location	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
Mühlhofan	0.045-0.135	0.015-0.225	2	0	0.36	0.04	
				7	0.29	0.03	
				14	0.17	0.02	
				28	0.12	0.02	
				35	0.11	0.01	
Italy 1991	0.081	0.0062	1	14	0.47	0.02	R-39
	0.16	0.012	1	14	0.57	0.03	
	0.094	0.0063	1	14	0.17	0.01	
	0.19	0.013	1	4	0.52	0.03	
	0.064	0.0064	1	14	0.07	<0.01	R-40
	0.13	0.013	1	14	0.19	<0.01	R-41
Japan 1988 (greenhouse)	0.2	0.005	1	14	0.38, 0.41	<0.005	R-42
				21	0.45, 0.41	0.01	
				30	0.36, 0.33	0.01	
				60	0.062, 0.058	0.007, 0.006	
Japan 1989 (greenhouse)	0.2	0.005	1	13	0.43 (2)	<0.005 (2)	R-43
				20	0.53, 0.5	<0.005 (2)	
				29	0.51, 0.49	0.01, 0.009	
		0.005	2	13	1.1, 1.2	0.015, 0.013	R-43
				20	1.1, 1.2	0.014 (2)	

Hops. Fenpyroximate 5% SC is registered for use on hops at dosage rates between 0.225 and 0.263 kg ai/ha in Germany, 0.05 kg ai/ha in Italy, and at 0.005 kg ai/hl in Japan. Several supervised trials were carried out on hops at rates between 0.375 and 0.75 kg ai/ha (1 application) in Germany, but only one, at 0.23 kg ai/ha, within the range covered by GAP. In this trial residues of fenpyroximate were <0.5-1.6 mg/kg in green hops and 1.2-4.3 mg/kg in dried hops 21 days after application. Residues of the *Z*-isomer were <0.05 and <1 mg/kg in green and dried hops respectively.

Table 23. Residues of fenpyroximate and its isomer in hops from supervised trials.

Country, Year, Location	Application			PHI, days	Residues in green and [dried] hops, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	Z- isomer	
Germany, 1989, Gambach	0.375	0.0125	1	0	5.2, 7.6	<0.5 (2)	R-44, R-45
				7	1.6, 3.8	<0.5 (2)	
				14	0.9, 3.1	<0.5 (2)	
				21	0.8, 3.2, [6.4], [<1]	<0.5 (2), [<1] (2)	
Oberrunseried	0.375	0.0086	1	0	2.7, 2.6	<0.5 (2)	R-46, R-47
				7	1.6, 1.1	<0.5 (2)	
				14	1.5, 1.1	<0.5 (2)	
				21	0.5, 0.8, [2.1], [2.1]	<0.5 (2), [<1] (2)	
Germany, 1990, Gambach	0.375	0.0188	1	0	3.1, 1.8	<0.5 (2)	R-48
				7	3.7, 2.1	<0.5 (2)	
				14	3.7, 2.5	<0.5 (2)	
				21	1.1, <0.5, [6.8, 8.2]	<0.5 (2), [<1] (2)	
Germany, 1990, Gambach	0.75	0.0375	1	0	11.6	<0.5	R-48
				7	11.3	<0.5	
				14	15.8	<0.5	
				21	10.4 [28.7]	<0.5 [1.7]	
Germany, 1990, Tannant Red	0.375	0.015	1	0	5.3	<0.5	R-48
				7	2.5	<0.5	
				14	2.4	<0.5	
				21	2.1, [7.0]	<0.5, [<1]	
Germany, 1990, Lindau-Bodenegg	0.375	0.0094	1	0	4.7	<0.5	R-48
				7	3.5	<0.5	
				14	13.7	<0.5	
				21	4.9, [<1]	<0.5, [<1]	
Germany, 1990, Lindau-Bodenegg	0.75	0.0188	1	0	25.9	<0.5	
				7	24.1	<0.5	
				14	12.1	<0.5	
				21	9.2, [25]	<0.5, [1.7]	
Germany, 1991	0.23	0.0075	1	0	11.3, 6.6, <0.5	<0.5 (3)	R.49
				7	1.5, 2.3, 2.6	<0.5 (3)	
				14	<0.5, 1.2, 1.7	<0.5 (3)	
				21	<u>≤0.5</u>, <u>0.7</u>, <u>1.6</u>, [1.2, 3.7, 4.3]	<0.5 (3), [<1] (3)	
Germany, 1991	0.46	0.015	1	0	9.8, 6.8, 14.7	<0.5 (3)	
				7	4.2, 4.0, 4.0	<0.5 (3)	

Country, Year, Location	Application			PHI, days	Residues in green and [dried] hops, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		Fenpyroximate	*Z*- isomer	
				14	1.3, 2.5, 2.3	<0.5 (3)	
				21	0.6, 1.5, 3.1, [2.5, 4.9, 3.6]	<0.5 (3), [<1] (3)	

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were provided.

In processing

Apples. Processing trials were carried out in Germany to determine residues of fenpyroximate and its *Z*- isomer in fruit, purée, cider, wet pomace and washings after two applications of fenpyroximate 5% SC at 0.075-0.08 kg ai/ha (Table 24). The last treatment was 21 days before harvest. The washed apples were finely chopped and cider was prepared using a household juice press. The cider was pasteurized at 75°C for 25 minutes. Other samples of washed apples were cut into small pieces and boiled for 20 minutes. Apple purée (mash) was separated from peel and pips using a sieve. Samples were analysed by GLC, using a nitrogen-selective detector (method DFG S 19, in accordance with GLP Guidelines). Recoveries were 79-92% for the active ingredient and between 71 and 88% for the *Z*- isomer (Burstell *et al*., 1992b).

Table 24. Residues of fenpyroximate and its isomer in apples and processed products.

Sample	Residues, mg/kg			
	Fenpyroximate		*Z*- isomer mg/kg	
	Trial 1 (0.075 kg ai/ha)	Trial 2 (0.08 kg ai/ha)	Trial 1	Trial 2
Fruit	0.06	0.15	<0.05	<0.05
Cider	<0.05	<0.05	<0.05	<0.05
Apple purée	<0.05	<0.05	<0.05	<0.05
Pomace, wet	0.13	0.39	<0.05	<0.05
Washings from apples	<0.05	<0.05	<0.05	<0.05
Washings from purée	<0.05	<0.05	<0.05	<0.05

Residues of fenpyroximate in the purée and cider were below the limit of determination, but were concentrated about twofold in wet pomace.

Grapes. Residues of fenpyroximate and its metabolite A (the *Z*- isomer) were investigated in grapes and wine.

In two trials on *Vitis vinifera* vines treated with fenpyroximate 5% SC at 0.18 kg ai/ha (Table 22, Trials R-34, 4-35), grapes collected 35 days after application and wine made from them were analysed by HPLC (Table 25).

Table 25. Residues of fenpyroximate and its isomer in grapes and wine from vines treated at 0.18 kg ai/ha.

Sample	Residues, mg/kg			
	Trial R-34		Trial R-35	
	Fenpyroximate	*Z*- isomer	Fenpyroximate	*Z*- isomer
Grape	0.15	<0.01	0.13, 0.14	<0.01
Wine	<0.01	<0.01	<0.01	<0.01

Fenpyroximate residues were reduced in wine. No data were provided on residues in raisin culls or raisin waste, which could be used as animal feed in some countries.

Hops. In trials in Germany hops treated at 0.46 and 0.75 kg ai/ha 21 days before harvest were used to brew beer. Residues were determined in dried hops, spent hops, yeast, sludge and beer. The results are shown in Table 26 (Secker, 1994).

Table 26. Residues of fenpyroximate and its isomer in processed products of hops.

Sample	Residues, mg/kg							
	Trial 1[1]		Trial 2[2]		Trial 3[2]		Trial 4[2]	
	Fenpyrox.	*Z*- isomer	Fenpyrox.	*Z*- isomer	Fenpyrox.	*Z*- isomer	Fenpyrox.	*Z*- isomer
Dried hops	37.4	1.2	6.4	<1.0	9.0	<1.0	11.4	<1.0
Sludge	4.7	0.4	1.0	0.2	0.9	0.1	1.6	0.2
Spent hops	5.8	0.4	0.8	0.2	1.4	<0.1	1.6	0.3
Yeast	0.4	<0.1	<0.1	<0.1	0.4	<0.1	0.4	<0.1
Beer	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01

[1] Treatment at 0.75 kg ai/ha
[2] Treatment at 0.46 kg ai/ha

The results show clearly that even at the exaggerated application rates (the maximum GAP rate is 0.263 kg ai/ha) no residues could be measured in beer. In yeast, which is of minor importance in the human diet, the highest residues of fenpyroximate were 0.4 mg/kg. In spent hops, which are used in animal feed, maximum combined residues of fenpyroximate and the *Z*- isomer were about 2 mg/kg from treatment at 0.46 kg/ha and 6 mg/kg from 0.75 kg/ha.

Residues in the edible portion of food commodities

The only data provided, apart from the processing trials just described, were on residues in orange pulp. These were all below 0.1 mg/kg.

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No information was provided.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs have been reported.

Country	Commodity	MRL, mg/kg
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)	1.0
	Apple	1.0
	Grapes	2.0
	Hops	15
Spain	Citrus fruits	0.3
	Pome fruits	0.3
	Grapes	0.3
Switzerland	Apple	0.2
	Grapes	0.2

APPRAISAL

The fate of fenpyroximate has been studied in rats, mandarins, apples, grapes, soil and water.

The principal metabolites identified are indicated below.

A: *tert*-butyl (*Z*)-Æ-(1,3,-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate
C: (*E*)-Æ-(1,3-dimethyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluic acid
F: 1,3-dimethyl-5-phenoxypyrazole-4-carbaldehyde
H: 1,3-dimethyl-5-phenoxypyrazole-4-carboxylic acid
K: 1,3-dimethyl-5-phenoxypyrazole-4-carbonitrile
L: *tert*-butyl (*E*)-Æ-(3-methyl-5-phenoxypyrazol-4-ylmethyleneamino-oxy)-*p*-toluate

Male and female rats were dosed orally once with fenpyroximate labelled with ^{14}C in both the pyrazole and benzyl rings at a 2 mg/kg or 400 mg/kg bw. Another group of animals received a daily dose of 2 mg/kg bw of the unlabelled compound for 14 days, followed by a single administration of [*pyrazole*-^{14}C]fenpyroximate at the same level. Fenpyroximate was rapidly excreted in the urine and faeces.

Following [*pyrazole*-^{14}C]fenpyroximate administration at 2 mg/kg, radioactivity was rapidly excreted in faeces and urine. After 168 hours, 70-85% of the dose had been excreted in the faeces and 12-18% in the urine. Negligible amounts of radioactivity were expired as CO_2 or volatile organic compounds. Similar results were obtained after multiple dosing with unlabelled fenpyroximate followed by a single dose of fenpyroximate at 2 mg/kg.

Although slower excretion was observed after a single administration at 400 mg/kg, 75-77% of the dose was excreted in the faeces and 11-12% in the urine after 168 hours. Tissue residues were generally low at 168 hours, and the highest concentration of radioactivity (1-4% of the dose) was in the gastrointestinal tract. The major urinary metabolites were 1,3-dimethyl-5-phenoxypyrazole-3-carboxylic acid (H) and 4-cyano-1-methyl-5-phenoxypyrazole-3-carboxylic acid. High levels of

unchanged fenpyroximate were present in the faeces, owing to the excretion of the unabsorbed compound.

A similar pattern of excretion and tissue distribution were observed after administration of [*benzyl*-^{14}C]fenpyroximate. The major urinary metabolite was terephthalic acid and large amounts of unchanged fenpyroximate were found in the faeces.

The principal metabolic pathways were isomerization, cleavage of the oxime ether bond between the benzyl and pyrazole rings, hydrolysis of the ester, oxidation of the *tert*-butyl group and *N*-demethylation of the pyrazole ring.

Low residues were found in the tissues: liver 0.1-0.25%; kidney 0.05-0.1 %; and fat 0.4-0.8% of the initial dose.

No metabolism studies were submitted for other animals.

The fate of residues in plants was studied in mandarins, apples and grapes, using [*pyrazole*-^{14}C] and [*benzyl*-^{14}C]fenpyroximate. Labelled fenpyroximate was applied to mandarins at approximately the recommended rate, and samples were collected at 0, 3, 7, 14, 28 and 137 days after treatment. Radioactivity was not detected in the pulp (LOD 0.03 mg/kg at 28 days and 0.004 mg/kg at 137 days after treatment). The radiocarbon concentration on and in treated leaves gradually decreased. Loss from the peel was slower. The half-life of fenpyroximate was 38.4 days in the peel and 8.8 days in the leaves. The principal ^{14}C residues were fenpyroximate and its *Z*- isomer, although *N*-demethyl-fenpyroximate was found at analytically significant levels in early trials on mandarins.

The *Z*- isomer (compound A) generally occurred at levels of ≤10% of those of fenpyroximate in the peel and leaves at short PHIs (3-7 days). *N*-demethyl fenpyroximate (compound L) occurred at comparable or slightly higher levels at PHIs of 28-137 days.

Labelled fenpyroximate was applied to apples at the maximum recommended field rate of 7.5 g ai/hl, and samples were analyzed at intervals. Fenpyroximate and its *Z*- isomer were the main ^{14}C residues in apples at harvest. Several metabolites were also found, but were of minor importance. The total radioactivity in the fruits decreased from 0.13 mg fenpyroximate equivalents/kg at day 0 to 0.003 mg/kg at day 57 (harvest).

Metabolism studies on grapes were carried out using pyrazole- and benzyl-labelled fenpyroximate. Fenpyroximate and its *Z*- isomer were again the main residues in grapes and stems at harvest. Several metabolites were detected at lower levels. After the application of labelled fenpyroximate at the recommended rate (37.5 g ai/ha) the highest total radioactivity found in grape bunches was 0.19 mg/kg fenpyroximate equivalents at day 7, and 0.08 mg/kg at day 57 (harvest).

In summary, plant metabolism studies indicated that the major residual compounds in crop commodities are unchanged fenpyroximate and its *Z*- isomer. Although the proportion of the *Z*-isomer increased with time, its residues were generally less than 20% of the fenpyroximate levels in fruits at PHIs up to 28 days. Leaves showed the same pattern of metabolites as fruits, but with higher levels of ^{14}C. Residues of *N*-demethyl-fenpyroximate (compound L) were of the same order as, or slightly higher than, those of the *Z*- isomer.

Although compounds A and L were the main metabolites in plants, compound A was a minor metabolite in animals and compound L was not found.

Studies of the fate of fenpyroximate in soil (sandy, silty and clay) showed that the degradation pathways consist of hydrolysis of the ester, isomerization or cleavage of the oxime group, *N*-

demethylation, oxidation of the methyl group at the 3-position on the pyrazole ring and hydroxylation of the phenyl ring, with final mineralization to CO_2. Compounds A, C, H and K were the major degradation products. The half-life was 10 to 50 days, except in sandy soil where it was 159 days. Fenpyroximate was strongly adsorbed to soil, to an extent depending on the content of soil organic matter.

The adsorption/desorption of [*pyrazole*-^{14}C]fenpyroximate was studied in four different soil types. The K_{oc} values were all 37,000 or more, showing that fenpyroximate is immobile in all the soils tested (loamy sand, sandy loam, clay loam and loam).

The leaching behaviour of fenpyroximate and its aged residues was studied in various soils. The results showed that small amounts of fenpyroximate move only through very sandy soils with low organic matter contents. The compound can therefore be classified as weakly mobile.

Environmental fate in water. The hydrolysis of fenpyroximate was studied in buffered sterile and unsterilized aqueous solutions at various Ph values and temperatures. Compounds A, C and F were identified as degradation products. The studies were too short to estimate half-lives.

The photolysis of fenpyroximate in solution was studied with irradiation by sunlight and a xenon lamp. The predominant product of photodegradation was compound A. Degradation was apparently by isomerization, oxime-ether cleavage and hydrolysis. The half-life was 2.6 days in sunlight and 1.5 hours under irradiation with a xenon lamp (603 watts, 290-300 nm) at pH 7.

The analytical methods for fenpyroximate and its isomer used in the reported studies were based on extraction with methanol or acetone, partitioning with hexane or acetonitrile, and clean-up on some combination of C_{18} cartridges, SX-3 gel, silica gel and alumina columns. Determination was by GLC or HPLC. The GLC methods determine fenpyroximate and its *Z*- isomer, while HPLC (with UV detection) determines fenpyroximate, its *Z*- isomer and *N*-demethyl-fenpyroximate in the same extract.

Recoveries of fenpyroximate and its *Z*- isomer from fruits were above 70% with LODs of 0.02-0.05 mg/kg. The limits of determination reported for other commodities were 0.1 mg/kg for dregs and yeast, 1 mg/kg for dried hops, 0.5 mg/kg for green hops, and 0.01 mg/kg for beer.

The storage stability of pyrazole-labelled fenpyroximate was investigated on apples and grapes stored at -20ºC. After about 3 years approximately 65% of the initial residue remained. In another study apples and grapes fortified with a solution of fenpyroximate and its metabolites were stored at -20ºC. The proportions of the original residues remaining in apples after 145 days were fenpyroximate 68%, *Z*- isomer 71%, and *N*-demethyl fenpyroximate 60%, and in grapes stored for 77 days fenpyroximate 76%, *Z*- isomer 87%, and *N*-demethyl-fenpyroximate 50%.

The stability of fenpyroximate residues at -20ºC was also studied in citrus samples (peel and pulp) fortified with fenpyroximate and its *Z*- isomer. The proportions of both compounds remaining were 65% in pulp stored for 140 days and 72% in peel stored for 188 days. Fenpyroximate and the *Z*-isomer were stable in hops (dried cones) stored at -18ºC for 2 years with about 100% of the residues remaining. The studies showed that fenpyroximate can be considered to be reasonably stable during these periods.

Results of residue trials were available for citrus (oranges and mandarins), apples, grapes and hops. For many trials only summary reports were supplied and few trials were according to GAP. Often representative chromatograms were not provided although control values and percentage recoveries were submitted.

Fenpyroximate is registered for use on citrus fruits in Brazil, Chile, Greece, Italy, Japan, Peru

and Spain with application rates from 0.1 to 0.2 kg ai/ha, and PHIs of 14-15 days. The Meeting received data from supervised trials in Brazil, Greece and Italy: residues were determined separately and the peel/pulp ratios were not reported. Supervised trials on mandarins treated at the recommended rate (0.005 kg ai/hl) were carried out in Japan in greenhouses, this being a minor use in that country. These trials were the only ones in which residues in the whole fruit were reported. Since the other trials showed that the residues occur principally in the peel and pulp:peel ratios were not reported, the Meeting could not estimate a maximum residue level.

Apples. Numerous field trials have been conducted in Australia, Belgium, France, Germany, Japan and New Zealand. No GAP was reported for Australia. A trial in Belgium was evaluated against GAP in France and Switzerland. Several trials in France and Germany were carried out according to GAP in those countries (0.008 kg ai/hl, 21 days PHI). In supervised trials in Japan fenpyroximate was applied at the recommended rate (0.005 kg ai/hl). The *Z*- isomer was determined in most of these trials and was below the limit of determination in almost every sample. Supervised trials according to GAP carried out in New Zealand showed parent residues from <0.01 to 0.13 mg/kg at the New Zealand PHI of 14 days; the *Z*- isomer was not determined. The storage period before analysis was not reported. The Meeting estimated a maximum residue level of 0.2 mg/kg.

Grapes. Supervised trials on vines were conducted in France, Germany, Italy and Japan. Those in France and Italy which approximated Portuguese GAP showed residues of <0.02 and 0.08 mg/kg (France) and 0.07, 0.17 and 0.47 mg/kg (Italy). Residues in two (greenhouse) trials in Japan in accordance with GAP were 0.38 to 0.53 mg/kg. Residues of fenpyroximate in all the trials complying with GAP ranged from <0.02 to 0.53 mg/kg. The Meeting concluded that the data were insufficient to estimate a maximum residue level for a major crop.

Hops. Results of nine German trials (1989-1991) were submitted to the Meeting, but only one trial was in accordance with GAP. The Meeting could not estimate a maximum residue level.

The Meeting received data from processing studies on apples. Residues of fenpyroximate in apple puree and cider were below the limit of determination. In two domestic processing trials with fruit containing 0.06 mg/kg and 0.15 mg/kg, the fenpyroximate residues in wet pomace were concentrated by factors ranging from 2.2 to 2.6. In the absence of the study details and because the studies did not represent a commercial process, the Meeting could not draw conclusions from the data.

Supervised trials on grapes were carried out in Germany to study the fate of fenpyroximate in processed products. Only summary reports were available, where critical supporting information was lacking. Residues of fenpyroximate in wine were below the limit of determination (<0.01 mg/kg), when made from grapes containing residues of fenpyroximate of 0.13-0.15 mg/kg. No data on processing to pomace were provided. In the absence of the study details the Meeting could not draw conclusions from the data.

Processing studies on hops showed that even with high fenpyroximate residues in the hops no residues could be detected in beer. A residue of 0.4 mg/kg was found in yeast, which is of minor importance in the human diet. The highest residue found in spent hops was 6 mg/kg, from dried hops with a fenpyroximate residue of 37.4 mg/kg.

No information was provided on residues of fenpyroximate occurring in commerce or at consumption.

Since metabolism studies showed that the *Z*- isomer was always less than 20% of the residue and in almost all supervised trials its residues were near the limit of determination, the Meeting concluded that the residue should be defined as fenpyroximate.

The Meeting considered the need to include livestock metabolism and animal transfer studies in accordance with FAO guidelines in future submissions. The Meeting was informed that animal studies were not available. Additional residue data on citrus fruits (oranges, whole fruit) with relevant information on GAP are needed, as are additional supervised trials data on grapes and hops reflecting GAP. Complete trial details should be provided, including the analytical methods used, validations thereof, and sample chromatograms.

RECOMMENDATIONS

The Meeting estimated a maximum residue level of 0.2 mg/kg for apples but this cannot be recommended for use as an MRL owing to the lack of critical supporting data.

FURTHER WORK OR INFORMATION

Desirable

1. An additional processing study on apples, conducted with apples containing residues at or above the estimated maximum residue level (0.2 mg.kg), reflecting commercial processing.

2. An additional study on processing grapes to wine and raisins, including data on by-products. Complete trial details should be provided.

3. Information on residues of fenpyroximate in foods in commerce or at consumption.

REFERENCES

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080102, R-01. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080103, R-02. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080202, R-03. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080203, R-04. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080302, R-05. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080303, R-06. Unpublished.

Iawamato, T. and Matano, O. 1993a. Residue determination of fenpyroximate in or on Satsuma mandarin treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, Japan and The Institute of Environmental Toxicology, Japan. Rep. No-4056, R-07. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000102, R-08. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000202, R-09. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000302, R-10. Unpublished.

Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000402, R-11. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000102, R-12. Unpublished.

Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000103, R-13. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080102, R-14. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080202, R-15. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080302, R-16. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080102, R-17. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080202, R-18. Unpublished.

Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080302, R-19. Unpublished.

Bull, M.S. and Holding, R.K. 1992. Residues of fenpyroximate and its metabolites (M1 & 12) in pome fruit following application of NNI-850. Ciba-Geigy, Australia. Rep. No. 92/12/1378, R-20. Unpublished.

Benet, F. and Decraecke, H. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans des pommes. ICI, France. Rep. No.RE-9205-H, R-21. Unpublished.

Benet, F. and Massenot, F. 1991a. Recherche de residus de fenpyroximate dans des pommes. ICI, France. Rep. No. RE-9109-H, R-22. Unpublished.

Benet, F. and Massenot, F. 1991b. Recherche de residus de fenpyroximate et de ses deux metabolites dans les pommes. ICI, France. Rep. No. RE-9117-H, R-23. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1991a. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I801, R-24. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1991b. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I811, R-25. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1992a. Investigation of residues in apples following a single application of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU812, R-26. Unpublished.

Burstell, H. Raquet, H. and Werner, H. 1992b. Investigation of residues in processed apples following two applications of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU801, R-27. Unpublished.

Iawamoto, T. and Matano, O. 1993b. Residue determination of fenpyroximate in or on apples treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4058, R-28. Unpublished.

Patterson, T.M., 1992. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.91/35B, R-29. Unpublished.

Patterson, T.M., 1994. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.93/35B, R-30. Unpublished.

Benet, F. and Massenot, F. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans du raisin et du vin. ICI, France. Rep. No. RE-9206-H, R-31. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020102, R-32. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, R-33. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU803020102, R-34. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, R-35. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU805020102, R-36. Unpublished.

Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU805020202, R-37. Unpublished.

Raquet, H. Werner, H.J. and Burstell, H 1994. Fenpyroximate (50 g/l) water miscible suspension concentrate. Investigation of residues in grapes following two applications of Hoe 094552. Hoechst Schering AgroEvo GmbH, Germany. Rep. No. ER91DEU814, R-38. Unpublished.

Sochor, H. 1994. Investigation of residues in vine grapes following one application of Hoe 094552. Hoechst, Germany. Rep. No.ER91ITA004, R-39. Unpublished.

Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080102, R-40. Unpublished.

Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080103, R-41. Unpublished.

Iawamoto, T. and Matano, O. 1993c. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Ishikawa- Japan

Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4059, R-42. Unpublished.

Iawamoto, T. and Matano, O. 1993d. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Fukui- Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4060, R-43. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030102, R-44. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030202, R-45. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030302, R-46. Unpublished.

Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030402, R-47. Unpublished.

Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER90DEU804, R-48. Unpublished.

Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER91DEU804, R-49. Unpublished.

Funayama, S., Kojima, Y. and Uchida, M. 1991. Liquid chromatographic determination of fenpyroximate in water. Nihon Nohyaku, Japan. Rep. No. ILSRE91-023A, Unpublished.

Galicia, H. & Wyss-Benz, M. 1992. ^{14}C-fenpyroximate (NNI-850) [pyrazole labeled]: Plant metabolism study in field grown apple. RCC Umweltchemie AG, Switzerland. Rep. No. RCC-274961, Unpublished.

Hirano, A., Izawa, Y., Funayama. S. and Uchida, M. 1990. Degradation of [pyrazole-^{14}C] and [benzyl-^{14}C] fenpyroximate in soils under laboratory condition. Nihon Nohyaku, Japan. Rep. No.ILSR-M-90-059A, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1990. Metabolism of fenpyroximate (NNI-850) in citrus. Nihon Nohyaku, Japan. Rep. No.ILSR-M-90060A, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1991a. Metabolism of [pyrazole-^{14}C] fenpyroximate (NNI-850) in citrus grown in the greenhouse. Nihon Nohyaku, Japan. Rep. No.ILSR-M-91-0190, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1991b. Metabolism of [benzyl-^{14}C] fenpyroximate (NNI-850) in citrus. Nihon Nohyaku, Japan. Rep. No.ILSR-M-91-020A, Unpublished.

Izawa, Y., Hirano, A., Funayama. S. and Uchida, M. 1993. Degradation of fenpyroximate in upland soils under laboratory conditions. J. Pesticide Sci., 18,67-75.

Krautter, G., Downs, J. and Lawrence, L. J. 1983. Metabolism of [14C]NNI-850 in tangerine trees under commercial conditions. PTRL, USA. Rep. No.1139. Unpublished.

Krautter, G., Downs, J. and Lawrence, L. J. 1989. Metabolism of [14C]NNI-850 in tangerine trees grown outside. PTRL, USA. Rep. No.1172. Unpublished.

McCann, D. J. 1992. Sorption/desorption of pyrazole-^{14}C-fenpyroximate on soils by batch equilibrium method. Battelle, USA. Rep. No SC910124. Unpublished.

NIHON NOHYAKU Co., Ltd. 1989a. Residue analysis of fenpyroximate and its metabolite in fruits (GLC method). Nihon Nohyaku, Japan. Rep. No. A-4001. Unpublished.

NIHON NOHYAKU Co., Ltd. 1989b. Residue analysis of fenpyroximate and its metabolite in fruits (HPLC method). Nihon Nohyaku, Japan. Rep. No. A-4002. Unpublished.

NIHON NOHYAKU Co., Ltd. 1989c. Residue analysis of fenpyroximate and its metabolite in fruits (GLC and HPLC method). Nihon Nohyaku, Japan. Rep. No. A-4003. Unpublished.

Nishizawa, H., Nakayama, M., Nakano, A., Susuki, T. and Uchida, M. 1990a. Hydrolysis of fenpyroximate in water. Nihon Nohyaku, Japan. Rep. No. ILSR-E-90056. Unpublished.

Nishizawa, H., Hirano, A., Hasegawa, T., Susuki, T. and Uchida, M. 1990b. Photodegradation of fenpyroximate in water. Nihon Nohyaku, Japan. Rep. No.ILSR-E-90-057A. Unpublished.

Nishizawa, H., Shigemura, M., Kitaura, T. and Uchida, M. 1992. Analytical method of fenpyroximate and its metabolites in soil. Nihon Nohyaku, Japan. Rep. No.ILSR-R92-001A. Unpublished.

Nishisawa, H., Motoba, K., Susuki, T., Ohshima, T. and Uchida, M. 1993. Metabolism of fenpyroximate in rats. J. Pesticide Sci., 18, 59-66.

Römbke, J. 1992. Determination of soil column leaching of fenpyroximate (normal study). Batelle, Germany. Rep. No. BE-ME-107-90-01-LEAS. Unpublished.

Römbke, J. and Brodesser, J. 1992. Determination of the degradation in soil of fenpyroximate. Batelle, Germany. Rep. No.BE-EM-107-90-01-SAB1.1. Unpublished.

Römbke, J. and Möllerfeld, J. 1992a. Determination of degradation and metabolism in soil of pyrazole-^{14}C-fenpyroximate. Battelle, Germany. Rep. No.BE-ME-107-90-01-SAB1. Unpublished.

Römbke, J. and Möllerfeld, J. 1992b. Determination of the

soil column leaching of pyrazole ^{14}C-fenpyroximate (aging study). Battelle, Germany. Rep. No.BE-ME-107-90-01-LEA3. Unpublished.

Römbke, J. and Möllerfeld, J. 1992c. Determination of the soil column leaching of benzyl-^{14}C-fenpyroximate (aging study). Battelle, Germany. Rep. No.BE-ME-107-90-01-LEA4. Unpublished.

Saxena, A. & McCann, D. 1992. Hydrolysis of pyrazole-^{14}C-fenpyroximate in buffered aqueous solutions. Batelle, USA. Rep. No.SC900192. Unpublished.

Sharp, D. E., 1991a. Metabolism and disposition of [pyrazole-^{14}C] NNI-850 in rats. Hazleton Laboratories America, Inc., USA. Rep. No. HLA 6283-102. Unpublished.

Sharp, D. E., 1991b. Metabolism and disposition of [benzyl-^{14}C] NNI-850 in rats. Hazleton Laboratories America, Inc., USA. Rep. No. HLA 6283-101. Unpublished.

Specht, W. 1992a. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in orange (pulp and peel). Dr. Specht & Partner, Germany. Rep. No. HOE 9039V, Az.77546A/90. Unpublished.

Specht, W. 1992b. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in apple (fruit, mash and cider). Dr.Specht & Partner, Germany. Rep. No. HOE 9032V, Az.77539A/90. Unpublished.

Specht, W. 1992c. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in vine (grape, cider and wine) Dr.Specht & Partner, Germany. Rep. No. HOE 9030V, Az.77537A/90. Unpublished.

Specht, W. 1992d. Validation of method DFG S 19 for the determination of the residue of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in processing products of hops (dregs, yeast and beer). Dr.Specht & Partner, Germany. Rep. No. HOE 92117V, Az.93232A/92. Unpublished.

Specht, W. & Winkelmann, 1987. Organochloride, organophosphorus, nitrogen-containing and other pesticides Gas-chromatographic determination after clean-up by gel permeation chromatography and silica gel minicolumn chromatography. In: Manual of pesticide residue analysis, edited by Thier, H. and Zeumer, H. Vol. 1, VCH publishers, New York.Swanson, M.B 1993. Direct photolysis of pyrazole-^{14}C-fenpyroximate in a buffered aqueous solution under artificial sunlight. Battelle, USA. Rep. No.SC910077. Unpublished.

Takemoto, Y., Funayama, S. and Uchida, 1990. Soil adsorption/desorption of fenpyroximate. Nihon Nohyaku, Japan. Rep. No.ILSR-M-90-058A. Unpublished.

Weber, H. 1993. Validation of method DFG S 19 for the determination of the residues of fenpyroximate (HOE 094552) and metabolite M-1 (HOE 112573) in soil. Dr. Specht & Partner, Germany. Rep. No. HOE 9236V, Az.96006A/92. Unpublished.

Weber, H. 1994. Storage stability of fenpyroximate (HOE 094552) and M-1 (HOE 112573) in hop (dried cone). Interim. report. Dr. Specht & Partner, Germany. Rep. No. HOE-9239, Az.96674/92. Unpublished.

Wyss-Benz, M. 1993a. Storage stability of ^{14}C-fenpyroximate (NNI-850) [pyrazole-labeled] in apples. RCC, Switzerland. Rep. No.RCC-358683. Unpublished.

Wyss-Benz, M. 1993b. Storage stability of ^{14}C-fenpyroximate (NNI-850) [pyrazole-labeled] in grapes. RCC, Switzerland. Rep. No.RCC-360000. Unpublished.

Wyss-Benz, M. and Mamouni, A. 1992a. 14C-fenpyroximate (NNI-850) [benzyl-labeled]: Plant metabolism study in field grown apples. RCC, Switzerland. Rep. No.RCC-274948. Unpublished.

Wyss-Benz, M. and Mamouni, A. 1992b. 14C-fenpyroximate (NNI-850) [pyrazole-labeled]: Plant metabolism study in field grown grape. RCC, Switzerland. Rep. No.RCC-274950. Unpublished.

Wyss-Benz, M. and Mamouni, A. 1992c. 14C-fenpyroximate (NNI-850) [pyrazole-labeled]: Plant metabolism study in field grown grape. RCC, Switzerland. Rep. No.RCC-274937. Unpublished.

Reports on residues from supervised trials

R-01. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080102, Unpublished.

R-02. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080103, Unpublished.

R-03. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080202, Unpublished.

R-04. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080203, Unpublished.

R-05. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080302, Unpublished.

R-06. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA013080303, Unpublished.

R-07. Iawamato, T. and Matano, O. 1993a. Residue determination of fenpyroximate in or on Satsuma mandarin treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, Japan and The

Institute of Environmental Toxicology, Japan. Rep. No-4056, Unpublished.

R-08. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000102, Unpublished.

R-09. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000202, Unpublished.

R-10. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000302, Unpublished.

R-11. Hoechst, 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90BRA004000402, Unpublished.

R-12. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000102, Unpublished.

R-13. Hoechst, 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER92GRC002000103, Unpublished.

R-14. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080102, Unpublished.

R-15. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080202, Unpublished.

R-16. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA008080302, Unpublished.

R-17. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080102, Unpublished.

R-18. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080202, Unpublished.

R-19. Hoechst, 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER90ITA009080302, Unpublished.

R-20. Bull, M.S. and Holding, R.K. 1992. Residues of fenpyroximate and its metabolites (M1 & 12) in pome fruit following application of NNI-850. Ciba-Geigy, Australia. Rep. No. 92/12/1378, Unpublished.

R-21. Benet, F. and Decraecke, H. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans des pommes. ICI, France. Rep. No.RE-9205-H, Unpublished.

R-22. Benet, F. and Massenot, F. 1991a. Recherche de residus de fenpyroximate dans des pommes. ICI, France. Rep. No. RE-9109-H, Unpublished.

R-23. Benet, F. and Massenot, F. 1991b. Recherche de residus de fenpyroximate et de ses deux metabolites dans les pommes. ICI, France. Rep. No. RE-9117-H, Unpublished.

R-24. Burstell, H. Raquet, H. and Werner, H. 1991a. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I801, Unpublished.

R-25. Burstell, H. Raquet, H. and Werner, H. 1991b. Investigation of residues in apples following application of Hoe 094552 for the control of spider mites. Hoechst AG, Germany. Rep No. DEU89I811, Unpublished.

R-26. Burstell, H. Raquet, H. and Werner, H. 1992a. Investigation of residues in apples following a single application of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU812, Unpublished.

R-27. Burstell, H. Raquet, H. and Werner, H. 1992b. Investigation of residues in processed apples following two applications of Hoe 094552. Hoechst AG, Germany. Rep No. ERDEU90DEU801, Unpublished.

R-28. Iawamoto, T. and Matano, O. 1993b. Residue determination of fenpyroximate in or on apples treated with fenpyroximate 5% SC at 50 ppm (ai). Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4058, Unpublished.

R-29. Patterson, T.M., 1992. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.91/35B, Unpublished.

R-30. Patterson, T.M., 1994. The analysis of apple for fenpyroximate residues. Ciba-Geigy New Zealand Limited, New Zealand. Rep. No.93/35B, Unpublished.

R-31. Benet, F. and Massenot, F. 1992. Recherche de residus de fenpyroximate et de ses deux metabolites dans du raisin et du vin. ICI, France. Rep. No. RE-9206-H, Unpublished.

R-32. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020102, Unpublished.

R-33. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, Unpublished.

R-34. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU803020102, Unpublished.

R-35. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU813020202, Unpublished.

R-36. Hoechst. 1991. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU805020102, Unpublished.

R-37. Hoechst. 1991. Report on plant residue trial.

Hoechst AG, Germany. Rep. No.ER89DEU805020202, Unpublished.

R-38. Raquet, H. Werner, H.J. and Burstell, H 1994. Fenpyroximate (50 g/l) water miscible suspension concentrate. Investigation of residues in grapes following two applications of Hoe 094552. Hoechst Schering AgroEvo GmbH, Germany. Rep. No. ER91DEU814, Unpublished.

R-39. Sochor, H. 1994. Investigation of residues in vine grapes following one application of Hoe 094552. Hoechst, Germany. Rep. No.ER91ITA004, Unpublished.

R-40. Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080102, Unpublished.

R-41. Hoechst. 1993. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER91ITA104080103, Unpublished.

R-42. Iawamoto, T. and Matano, O. 1993c. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Ishikawa- Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4059, Unpublished.

R-43. Iawamoto, T. and Matano, O. 1993d. Residue determination of fenpyroximate in or on grapes treated with fenpyroximate 5% SC at 50 ppm (ai)-Fukui- Japan Plant Protection Association, and The Institute of Environmental Toxicology, Japan. Rep. No.R-4060, Unpublished.

R-44. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030102, Unpublished.

R-45. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030202, Unpublished.

R-46. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030302, Unpublished.

R-47. Hoechst. 1992. Report on plant residue trial. Hoechst AG, Germany. Rep. No.ER89DEU804030402, Unpublished.

R-48. Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER90DEU804, Unpublished.

R-49. Sochor, A. 1994. Fenpyroximate, water miscible suspension 50 g/l. Investigation of residues in processed and no processed hops following one application. Hoechst, Germany. Rep. No. ER91DEU804, Unpublished.

FENTHION (039)

EXPLANATION

Fenthion was first evaluated in 1971 and has been reviewed several times since, most recently in 1989. It was proposed for periodic review by the CCPR in 1991 (ALINORM 91/24A, Appendix VI para 18).

The 1992 CCPR was informed that fenthion was still used in many countries on a variety of crops and that substantial data could be made available in time for review by the 1995 Joint Meeting (ALINORM 93/24, para 241 and Appendix V).

New information was made available to the Meeting on residues of fenthion from supervised trials on cherries in Germany, peaches in South Africa and Spain, mandarins and oranges in Spain, olives in Spain, Greece and Italy, rice in Japan and mangoes, rockmelons, cucumbers, zucchini, capsicum peppers and tomatoes in Australia. Data were also supplied from supervised trials on cattle (lactating and non-lactating), pigs and sheep, on animal and plant metabolism, environmental fate, analytical methods, and the stability of fenthion residues in stored analytical samples.

Information on registered use patterns was received from Australia, Canada, New Zealand, The Netherlands, Peru and the sponsor. A summary of world-wide GAP was provided by the sponsor.

IDENTITY

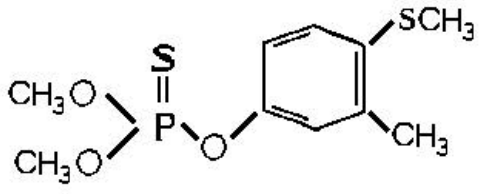
ISO common name: fenthion

Chemical name:

IUPAC: *O,O*-dimethyl *O*-4-methylthio-*m*-tolyl phosphorothioate
CA: *O,O*-dimethyl *O*-[3-methyl-4-(methylthio)phenyl] phosphorothioate

CAS No: 55-38-9
CIPAC No: 79
Synonyms: MPP; mercaptophos; OMS 2; ENT 25540

Structural formula:



Molecular formula: $C_{10}H_{15}O_3PS_2$
Molecular weight: 278.3

Structural formulae of the principal metabolites and degradation products of fenthion are shown in

fenthion

Figure 1. The structures of fenthion phenol sulfoxide â-glycoside, fenthion phenol sulfone â-glycoside, *O*-methylfenthion phenol sulfone, fenthion phenol sulfonic acid, and 3-methylphenol are not shown.

Physical and chemical properties

Pure active ingredient

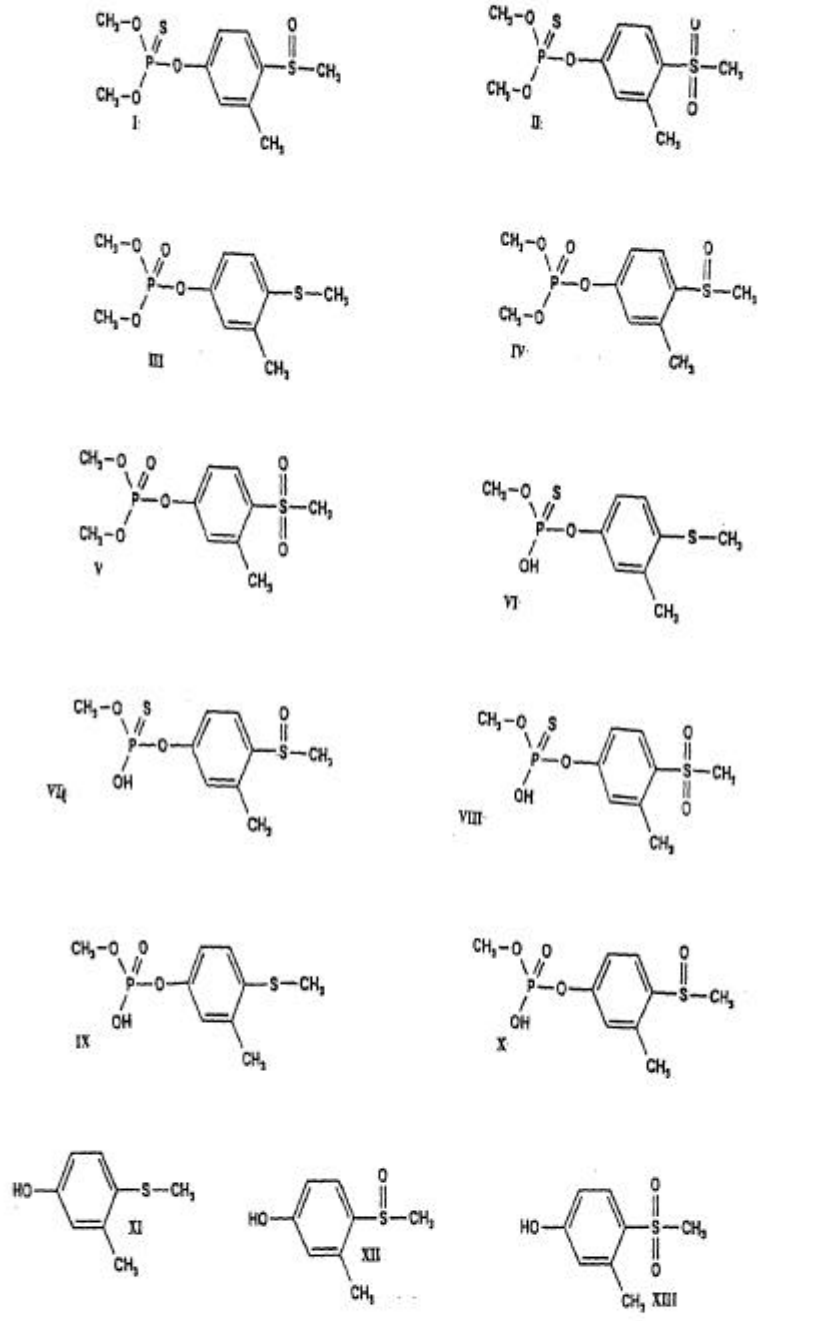
Vapour pressure:	3.7×10^{-4} Pa at 20°C (extrapolated)	
	7.4×10^{-4} Pa at 25°C (extrapolated)	
Octanol/water partition coefficient: log P_{OW} = 4.84		
Solubility at 20°C:	water	4.2 mg/l
	n-hexane	100 g/l
	xylene	>250 g/l
	1,2-dichloroethane	>250 g/l
	2-propanol	>250 g/l
	1-octanol	>250 g/l
	polyethylene glycol (lutrol)	>250 g/l
	acetone	>250 g/l
	acetonitrile	>250 g/l
	ethyl acetate	>250 g/l
	dimethylsulfoxide	>250 g/l
Relative density:	D_4^{20} = 1.25	
Hydrolysis:	at pH 7 and 25°C half-life >40 days	
Photolysis:	half-lives of 4.5-29 minutes in water at 23-25°C	

Formulations

Fenthion is sold as DP, EC, GR, PO, SA, SO, and WP formulations.

fenthion

Figure 1. Structures of principal metabolites and degradation products of fenthion.



I Fenthion sulphoxide
II Fenthion sulphone
III Fenthion oxygen analogue
IV Fenthion oxygen analogue sulphoxide
V Fenthion oxygen analogue sulphone
VI Demethylfenthion
VII Demethylfenthion sulphoxide
VIII Demethylfenthion sulphone
IX Demethylfenthion oxygen analogue
X Demethylfenthion oxygen analogue sulphoxide
XI Fenthion phenol
XII Fenthion phenol sulphoxide
XIII Fenthion phenol sulpone

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Studies on metabolism by rats, rabbits, cattle, pigs and goats were made available to the Meeting.

Rats. Male rats were given a single oral or single and multiple peritoneal doses of ^{32}P-labelled fenthion (Brady and Arthur, 1961). One group (18 rats) was dosed intraperitoneally at 10 mg/kg body weight/day for 10 consecutive days. Urine and faeces were collected over that and the following 10-day period. Animals were killed at 1, 3, 7, 10, 13 and 20 days after beginning the experiment. Liver, kidneys, heart, skin, bone and muscle were analysed for total radioactivity. Acetonitrile-soluble radioactive residues in the tissues were below the limit of determination of the radioassay method (<0.05 mg/kg) after 3 days. Fenthion and its oxidative metabolites were shown not to be stored in tissues. The increasing incorporation of radiolabelled phosphorus into bone showed that ready degradation of fenthion had occurred. Eighty per cent of the administered dose was eliminated by 20 days after the first injection (approximately 60% in the urine, 20% in the faeces).

A second group of 2 rats was given a single intraperitoneal treatment with 200 mg/kg bw of labelled fenthion and killed 1.5 hours later when signs of poisoning were apparent. The concentration of the radiolabel (acetonitrile-soluble, fenthion equivalents) in several tissues was determined. The highest levels were in the liver (29.5 mg/kg), kidneys (26.9 mg/kg), muscle (9.6 mg/kg), heart (9.6 mg/kg) and skin (6.1 mg/kg).

A third group of 4 rats was given a single oral dose by stomach tube of 100 mg/kg bw. Rats were killed on the third and seventh day after treatment. Urine and faeces were collected throughout and both total and chloroform-soluble ^{32}P were determined. Tissues by the third day contained less than 0.01 mg/kg fenthion equivalents of chloroform-soluble material, except liver which contained 0.2 mg/kg. No acetonitrile-soluble material was detected in the blood, brain or fat. Fenthion was readily oxidized by the rats to give fenthion oxygen analogue (fenthion oxon) and the sulfones and sulfoxides of fenthion and fenthion oxon. The rats excreted 86% of the administered dose by 7 days after treatment (approximately 46% in the urine and 40% in the faeces).

From 96 to 99% of the radiolabel in the urine and faeces was asscoiated with hydrolysis products by 3 days after treatment. *O,O*-dimethyl hydrogen phosphorothioate was the major product in the urine and dimethyl hydrogen phosphate in the faeces. Only a small percentage of the radiolabelled material in the faeces and urine was organosoluble. In the urine, chloroform-soluble radioactivity made up about 4% of the total and contained fenthion oxon sulfoxide and sulfone as the major components (approximately 87% at days 1 and 2 and 57% at day 3). Fenthion, fenthion sulfoxide and fenthion sulfone were present at much lower levels, generally of the order of 5% of the chloroform-soluble radioactivity. Fenthion oxon was present at <5% at days 1 and 2 but accounted for 21% of the total chloroform-soluble activity at day 3.

Female rats (24, divided into 3 groups fed different dietary regimes: high energy, high energy plus oil supplement and low energy) were given a single dose of ^{35}S-labelled fenthion at 25 mg/kg bw, either subcutaneously or orally, and the animals were killed after 30 hours for tissue collection (Begum, 1967). Urine and faeces were collected throughout.

In the orally-treated rats, maximum levels of radioactivity in the blood occurred after 9 hours in the high-energy diet group (54 mg/kg fenthion equivalents) and 1 hour in the low-energy group (59.4 mg/kg). These levels decreased to 9 and 8 mg/kg respectively after 30 hours. In subcutaneously-treated rats, maximum blood levels were after 9 hours (34.3 mg/kg, high-energy diet) and 1 hour (58.7 mg/kg, low-energy diet). After 30 hours, blood levels had declined to about 5 mg/kg in both groups of animals. The presence of an oil supplement had no marked effect on the levels found in the blood.

In all groups elimination was primarily in the urine, with the average amount of radiolabel eliminated being between 16 and 21% of the oral dose and 22 and 24% of the subcutaneous dose. In the faeces, 1 to 3% of the total dose administered had been eliminated after 30 hours, the route of administration not having a significant effect. The metabolites found in the urine from both the orally and subcutaneously treated rats were mainly water-soluble products (97.5-99% of the ^{35}S label in the urine after 30 hours), which were not identified. In the urine, fenthion sulfoxide and fenthion oxon sulfoxide and sulfone were the principal chloroform-soluble compounds (approximately 99% of the radioactive material at 30 hours). Smaller amounts of fenthion, fenthion sulfone and fenthion oxon (never more than 10% between 6 and 24 hours and <1% at 30 hours) were also detected. Most of the radiolabel found in the faeces was benzene-soluble and fenthion was the principal component, making up 78% of the total radiolabel present after 30 hours. Fenthion oxon was the other compound of significance found in the faeces (14-16% of the total radiolabel at 30 hours). Fenthion sulfoxide and sulfone and fenthion oxon sulfoxide and sulfone were present in amounts below 5% of the total administered dose at 30 hours.

In the tissues, residues of ^{35}S-fenthion or its metabolites were detected in the liver (oral 8.6-11.4 mg/kg, subcutaneous 7.6-12.6 mg/kg fenthion equivalents), kidneys (4.2-6.4 and 6.3-9.4 mg/kg respectively) and heart (2-4 and 0.8-3.1 mg/kg). No major difference was noted between the residue levels in orally and subcutaneously treated animals. Fenthion was the predominant radioactive compound identified in all tissues (29.2-33.1% of the radioactive acetonitrile-soluble material isolated). Fenthion oxon and its sulfoxide and sulfone were also major unhydrolysed metabolites in the livers and kidneys, in which fenthion sulfone and, to a lesser extent, fenthion sulfoxide were minor metabolites. In the heart only fenthion and fenthion oxon sulfoxide and sulfone were identified.

Four groups of Wistar laboratory rats (5 male and 5 female rats/group) were treated with fenthion labelled with ^{14}C at the 1-phenyl position (Puhl and Hurley, 1982). The groups were treated as follows.

Group A: single intravenous dose of 2 mg/kg bw.
Group B: single oral dose of 10 mg/kg bw (low, non-toxic, dose)
Group C: fourteen daily oral doses of unlabelled fenthion followed by one oral dose of radiolabelled fenthion. All doses were 10 mg/kg bw.
Group D: single oral dose of 100 mg/kg bw (toxic level).

Oral doses were administered directly into the stomach. Intravenous doses were injected into the tail vein. The animals were killed 72 hours after the final dose for tissue collection and analysis. Urine and faeces were collected throughout.

Excretion of the radiolabel in all groups was chiefly in the urine (after 72 hours >90% of the ^{14}C dose was recovered). Faeces contained between 2 and 6% of the recovered ^{14}C, while tissues had <2%. No radioactivity was detected in expired gases. Total recoveries of the administered radiolabel were between 94 and 110%. Excretion rates in male and females rats had reached plateau values of >90% of the administered dose by 24 hours, except in the high-dose group which took about 48 hours to reach a plateau. The radiolabel remaining in the body after 72 hours was less than 2% of the recovered dose.

Tissue levels were generally low (<0.1 mg/kg as fenthion equivalents) in Groups A, B, and C except in fat (0.12 mg/kg mean) and gonads (0.11 mg/kg mean) from Group C females. In Group D residues were higher, with fat containing the highest levels (mean values of 0.77 mg/kg in males and 3.4 mg/kg in females), but only in proportion to the increased dose.

Male and female rat metabolism was similar with no major differences in distribution. In the urine identified metabolites were found to account for more than 90% of the total recovered ^{14}C. Fenthion phenol, its sulfoxide and sulfone, including their sulfate and glucuronide conjugates, were the

major metabolites (approximately 60% of the total ^{14}C recovered in the urine, faeces, and bodies in groups A-C and 30-40% in group D). Demethyl metabolites made up approximately 30% of the recovered ^{14}C (30-50% in group D). Fenthion was detected only in the faeces at levels below 1.5% of the total ^{14}C recovered. Fenthion oxon sulfoxide accounted for 1-4.5% of the ^{14}C recovered from the urine. The faeces contained less than 3% of the total ^{14}C recovered: fenthion, the phenol sulfone, and the phenol sulfoxide were all identified, each at levels below 1.5% of the recovered ^{14}C.

Sprague Dawley Wistar rats were dosed orally or intravenously (i.v.) according to the treatment regimes shown in Table 1 in a study which complied with GLP (Doolittle and Bates, 1993).

Table 1. Regimes for treating rats with radiolabelled fenthion (Doolittle and Bates, 1993).

Group	No. of rats[1]	Dose			Termination (hours)	Purpose
		Route	mg/kg bw	No.		
1	4	oral	0.3	1	72	$^{14}CO_2$, tissue distribution
2	10	oral	0.3	1	168	tissue distribution
3	10	oral	1.5	1	168	tissue distribution
4	10	iv	0.125	1	24,72,168	tissue distribution
5	10	oral	0.3	15[2]	168	tissue distribution
6	12	oral	1.5	1	na	cholinesterase

[1] Each group contained an equal number of males and females
[2] Unlabelled fenthion for 14 days, then one dose of [^{14}C]fenthion

All the rats eliminated most of the [^{14}C]fenthion in the urine, with a little faecal elimination. About 80% of the administered radiolabel was recovered in the urine of the orally treated rats and 100% in that from the i.v. group by 24 hours after dosing. The faeces contained about 2-3% of the administered radiolabel (about 8% in group 3). The cumulative elimination via the urine increased rapidly and had reached constant levels by about 24 hours, except in group 5 which required about 48 hours. The pattern in the faeces was similar. Cage rinses accounted for less than 1% of the total dose in all groups and no $^{14}CO_2$ was found.

Levels of the radiolabel in tissues and organs were below the limit of detection (0.001 mg/kg fenthion equivalents) in groups given single oral doses. Residues in the iv group were also undetectable except in one fat sample containing 0.001 mg/kg . Animals treated orally for 15 days had levels of 0.001 mg/kg in bone, 0.002 mg/kg in fat, 0.004 mg/kg in the spleen, 0.005 mg/kg in the carcase and 0.07 mg/kg in the lung. Tissue and carcase residues on average accounted for less than 1% of the total dose administered. The samples anaylysed were bone, brain, carcase, fat, heart, kidneys, liver, lung, muscle, ovary, spleen, uterus, testes and whole blood.

The total ^{14}C recovered in the urine, faeces, cage rinses, tissues, carcase and CO_2 was measured. Most of the administered radiolabel (77-100%) was recovered in the urine in all groups. Levels recovered in the faeces ranged from 2 to 8% of the administered dose. Levels of radiolabel in the tissues were ≤0.01% of the administered dose except in group 5 where approximately 0.2% of the dose was recovered, of which 0.16% was in the lung. More than 98% of the recovered radiolabel was in the urine, faeces and cage washes, showing effective elimination of fenthion in all the treatment groups.

Fenthion phenol and its sulfoxide and sulfone were the major metabolites identified in the urine (pooled by sex) from the orally treated rats 4-24 hours after treatment. Fenthion oxon was tentatively identified. Table 2 shows the results.

Table 2. Major metabolites found in pooled rat urine (4-24 hours) after oral treatments with [1-^{14}C-*phenyl*]fenthion and their overall average proportions (Doolittle and Bates, 1993).

Metabolite	Mean % of total residue
Ethyl acetate mobile phase	
Fenthion phenol sulfoxide	21.8
Fenthion phenol sulfone	25.9
Fenthion phenol	11.9
Fenthion oxon sulfoxide	4.1
Benzene/methanol mobile phase	
Fenthion phenol sulfoxide	25.4
Fenthion phenol sulfone	21.5
Fenthion phenol	12.1
Fenthion oxon sulfoxide	3.5

The oxon was tentatively identified in group 5 males (11.5% of the total residue) and females (18.7%) in analyses with the benzene/methanol mobile system. An overall average of 63.1% of the total residue was recovered with the ethyl acetate mobile phase and 63.3% with the benzene/methanol.

Serum cholinesterase activities were lower 24 hours after dosing than in the untreated control rats, but were comparable to the controls after 72 and 168 hours.

Rabbits. Male and female rabbits fed on low or high calorie diets were dosed by subcutaneous injection (four rabbits) or orally (five rabbits) with [^{35}S]fenthion at 25 mg/kg bw and killed after 30 hours for tissue collection (Begum, 1967). Blood, urine and faeces were collected throughout.

In the orally-treated rabbits, maximum levels of ^{35}S in the blood occurred after 9 hours (57.8 mg/kg fenthion equivalents, high-energy diet) and 3 hours (81.2 mg/kg, low-energy diet) and decreased to 2.8 and 0 mg/kg respectively after 30 hours. In the injected rabbits the maximum blood levels were at 6 hours (77.3 mg/kg, high-energy diet) and 1 hour (78.3 mg/kg, low-energy diet). After 30 hours blood levels had declined to 14.2 and 11.8 mg/kg respectively. The presence of an oil supplement had no marked effect on the levels.

Excretion in the urine was 10.6-25% of the applied radiolabel after 30 hours in the rabbits treated orally and 12.1-17.2% after 24 hours in those injected. At all times after both treatments, approximately 90% or more of the ^{35}S was water-soluble. Elimination of the ^{35}S in the faeces was never more than 1%.

The main unhydrolysed metabolites in the urine after 30 hours were fenthion oxon sulfone (approximately 11-22% of the metabolites) and sulfoxide (approximately 70-77%) and fenthion sulfoxide (approximately 7-10%). Fenthion, fenthion sulfone and fenthion oxon were minor components (<7.5% throughout the 30-hour period). In the faeces, fenthion was the principal compound throughout and after 30 hours it accounted for about 70% of the total radiolabel. Fenthion oxon was also a major component (18-20% at 30 hours), with other unhydrolysed metabolites (fenthion sulfone and sulfoxide, and the oxon sulfone and sulfoxide) amounting to less than 6% of the total administered doses.

In tissues, residues of [^{35}S]fenthion or its metabolites were detected in the liver (approximately 9-13 mg/kg expressed as fenthion, orally and subcutaneously treated animals), kidneys (approximately 6-10.5 mg/kg) and heart (approximately 2-4.5 mg/kg). No major difference between the residue levels in orally and subcutaneously treated animals was noted. Fenthion was the major residue found in the liver

and kidneys (approximately 45% and 33%), where fenthion sulfoxide and sulfone and the oxon sulfoxide and sulfone were also detected in varying amounts. In the heart the major compounds were fenthion (28-30%), the oxon sulfone (21-22%) and the oxon sulfoxide (42-50%), but neither fenthion sulfone nor fenthion oxon was detected.

Cattle. [^{32}P]fenthion was administered dermally to two lactating Jersey cows (0.5% emulsion, 1 litre/cow, cows about 360 kg each, approximately 14 mg/kg bw), and two other lactating Jersey cows (about 400 kg each) were injected intramuscularly with 3.5 g of the radiolabelled material, equivalent to about 9 mg/kg bw (Knowles and Arthur, 1966). Faeces, milk and urine were collected throughout and the cows were killed 14 days after dermal treatment and 21 days after i.m. treatment. Liver, muscle, fat, skin and injection site samples were collected.

In the urine from both treatment groups, peak concentrations of radioactivity were on the day after treatment. In the i.m. group the total ^{32}P in the urine decreased from 33 mg/kg fenthion equivalents at day 1 to 1.6 mg/kg at day 21. More than 95% of the radiolabel in the urine was associated with hydrolysis products, with dimethyl phosphorothioate and dimethyl phosphate as major metabolites. The remainder of the label was organosoluble and fenthion sulfone or oxon sulfoxide or sulfone were the major metabolites. Faecal elimination was minor with cumulative levels of 3.7% of the administered dose (dermal) and 4.1% (intramuscular) and peak values of 2.3 mg/kg (dermal) and 5.8 mg/kg (intramuscular) after two days.

In the tissues the highest level of the radiolabel was found in the liver (0.44 mg/kg fenthion equivalents) with the acetonitrile-soluble radioactivity being below 0.001 mg/kg from the dermal treatments and less than 30% of the total radiolabel in the liver from the i.m. Table 3 shows the residues in the tissues.

Approximately 1% of the dermal dose and 2% of the intramuscular dose were eliminated in the milk. Peak levels were at 18 hours after the dermal treatments (0.67 mg/kg fenthion equivalents total, 0.25 mg/kg acetonitrile-soluble) and 8 hours after the intramuscular (1.1 mg/kg total, 0.53 mg/kg acetonitrile-soluble). At 5 days the total radiolabel was 0.32 mg/kg from the dermal and 0.63 mg/kg from the i.m. treatments of which 0.009 and 0.02 mg/kg respectively was acetonitrile-soluble. The residues at day 7 from the dermal treatments were 0.26 mg/kg (total) and <0.001 mg/kg (acetonitrile-soluble). At 14 days after intramuscular treatment the milk contained 0.21 mg/kg fenthion equivalents of which 0.014 mg/kg was acetonitrile-soluble. Fenthion made up approximately half the milk residue with fenthion sulfone and fenthion oxon sulfoxide and sulfone constituting a second major fraction. Fenthion sulfoxide and fenthion oxon were minor metabolites.

Table 3. ^{32}P in cow tissues at slaughter 14 days after treatment with [^{32}P]fenthion (Knowles and Arthur, 1966).

Sample	^{32}P as fenthion equivalents, mg/kg			
	Dermal treatment		Intramuscular treatment	
	Total	CH_3CN-soluble	Total	CH_3CN-soluble
Muscle	0.03-0.04	<0.001	0.1-1	0.02-0.38
Subcutaneous fat	0.01-0.05		0.16-0.3	0.08-0.2
Omental fat	0.041	<0.001	0.56	0.15
Liver	0.44	<0.001	3.3	0.76
Skin	0.49	0.075		
Injection site			164	76.5

[^{32}P]Fenthion was given to two dairy cows orally by capsule at the rate of approximately 1.5 mg/kg bw for 14 days (Everett, 1963). The animals were killed 7 days after the last dose for tissue analysis. Two other dairy cattle were treated daily by backrubber application for 7 days with 50 ml of a 1% solution of [^{32}P]fenthion and killed seven days after the last treatment. Samples of milk were taken throughout both experiments. The amount of fenthion administered was calculated on the basis that all the fenthion used at the rate of 0.1 lb/acre for mosquito control had drifted on to pasture.

The highest residues in the milk (acetonitrile-soluble) in the feeding trial were 0.24 mg/kg after 2 days in one cow and 0.36 mg/kg after 13 days in the other. Within 2 days of stopping treatment they were <0.01 mg/kg in both animals. In the backrubber trials, acetonitrile-soluble residues peaked at 0.15 mg/kg after 4 days in one cow and 0.47 mg/kg after 6 days in the other. Three to five days after the cessation of treatment, residue levels were <0.01 mg/kg in the milk of both cows. Residues in the tissues from both treatments were similar and were reported as total residues of fenthion and metabolites. Subcutaneous fat had the highest levels from the backrubber treatment (0.14 and 0.26 mg/kg). Omental and renal fat levels were <0.1 mg/kg. Residues in the kidneys and liver were approximately 0.02 mg/kg and in muscle ≤0.01 mg/kg. In the feeding study the highest residues were in the kidneys and liver at 0.02-0.04 mg/kg. Levels in the fat were 0.01-0.02 mg/kg and in muscle 0.006-0.01 mg/kg. Eighty-two to ninety-six per cent of the radiolabel was identified as being in fenthion or its metabolites.

A lactating Jersey cow (408 kg) was given a single dermal treatment (backline - top of shoulders to base of tail) with [1-^{14}C-*phenyl*]fenthion at 5.08 mg/kg (Krautter, 1990a). Milk, faeces and urine were collected until the animal was killed 18 hours after treatment. Hair, skin, subcutaneous fat, kidneys, liver and muscle were analysed. Milk production and feed and water consumption did not appear to be adversely affected over the trial period.

The mean ^{14}C residues as fenthion equivalents were treatment site hair 16,200 mg/kg; non-treatment site hair 2.3 mg/kg, treatment site skin 106 mg/kg; non-treatment site skin 0.1 mg/kg; subcutaneous fat at treatment site 6.1 mg/kg, at an untreated site 1.8 mg/kg; peritoneal fat 0.3 mg/kg; liver 0.1 mg/kg; kidneys 0.1 mg/kg; muscle 0.3 mg/kg. The total mean residues in the milk were 0.03 mg/kg 6 and 18 hours after treatment and 0.05 mg/kg 12 hours after treatment. In the urine the mean radiocarbon level was 3.9 mg/kg fenthion equivalents.

Extraction efficiencies from the tissues were all greater than 90% except from skin where an average extraction of 29% was recorded. Recoveries after frozen storage were satisfactory for fat (102%) and muscle (about 70%). Recoveries from kidneys and liver were about 25% (See the section "Stability of pesticide residues in stored analytical samples" for further comments on sample stability).

Fenthion was the major component (typically >90%) of the radiolabel in all tissues except the liver and kidneys where it was 71 and 51% respectively. Fenthion sulfoxide was the source of up to 5% of the radiocarbon in the hair, skin, muscle and fat but was not present in the kidneys or liver, which contained significant amounts of unidentified polar metabolites (44 and 22% respectively). About 5% of the total radioactivity in the liver and about 18% in the kidneys could be extracted into water and was tentatively identified as being from glucuronide conjugates of fenthion phenol sulfoxide and/or sulfone (Krautter, 1990b).

Goat. A lactating goat was dosed orally by capsule once daily for three consecutive days with 1-[^{14}C]-phenyl-labelled fenthion at 20 mg/kg bw and slaughtered 3.5 hours after the final dose for tissue analysis (Weber and Ecker, 1992). Milk, plasma and excreta were collected throughout. Approximately 52% of the administered ^{14}C was recovered: urine 44%, faeces 6.3%, milk 0.2% and edible tissues an estimated 1%. A large part of the final dose remained unquantified in the animal's gastrointestinal tract. Plasma levels peaked within 2-4 hours after dosing. A half-life of about 3 hours in the plasma was calculated for the first dose with the mean residence time being 6.4 hours.

Levels of ^{14}C as fenthion equivalents in the tissues and organs were liver 3.3 mg/kg; kidneys 24.1 mg/kg; muscle 0.6 mg/kg; and fat 2.7 mg/kg perirenal, 1.1 mg/kg subcutaneous and 1 mg/kg omental. Residues of fenthion sulfoxide and fenthion sulfone in the fat totalled approximately 0.5 mg/kg (0.3 mg/kg of the sulfoxide, 0.2 mg/kg of the sulfone) supporting a description of the residue as "fat-soluble". In milk the residue level was approximately 3 mg/kg 8 hours after the first and second doses. Detailed results are shown in Table 4.

During storage for an unspecified time at about -20°C further degradation (mainly oxidation and/or hydrolysis) occurred with a consequent increase in the amount of demethylated, oxidized and dephosphorylated residues. Further information on storage stability is provided in the "Stability of pesticide residues in stored analytical samples" section.

In urine, 56% of the radioactivity was associated with fenthion phenol and its sulfoxide and sulfone. Demethylated P=S compounds (demethylfenthion and its sulfoxide and sulfone) made up approximately 29% of the renal radioactivity. Eleven per cent of the radioactivity was associated with demethylated P=O compounds (demethylfenthion oxon and its sulfoxide).

Pigs. A male and female Duroc pig (each approximately 15 kg) were given a single oral dose of 5 mg/kg bw of [1-^{13,14}C-*phenyl*]fenthion. One week later, the female pig was dosed with the radiolabelled material at the rate of 10 mg/kg bw per day for two consecutive days and the male pig treated similarly for 3 consecutive days (Pither, 1979). Urine and faeces were collected throughout. Blood samples were taken after the first of the multiple doses. The male pig was killed 6 hours after the last dose (at the residue peak in whole blood) and the female pig 30 hours after the last dose. Tissues were then collected and analysed for radiocarbon.

Table 4. Compounds identified in tissues and milk from a goat dosed with [1-^{14}C-*phenyl*]fenthion(Weber and Ecker, 1992).

Compound[1]	^{14}C expressed as mg/kg fenthion equivalents and as % of total ^{14}C in the sample											
	Liver		Kidneys		Muscle, thigh		Muscle, flank[2]		Fat, composite		Milk, composite[3]	
	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%	mg/kg	%
FSO	0.8	23	15	64	0.1	15	0.2	26	0.5	33	0.6	21
FPOSODM	0.3	19	2	8	0.2	37	0.2	34	-		0.4	16
FSO2	0.3	11	6	24	-		<0.1	12	0.2	12	1.4	44
FPSSODM	0.5	8	0.6	3	<0.1	6	<0.1	6	0.1	7	0.1	4
FPSSO2DM	0.4	6	0.3	1	<0.1	6	<0.1	6	0.2	11	0.1	3
FPOSDM	0.2	5	-	-	<0.1	8	<0.1	8	-		<0.1	1
FS	<0.1	1	-	-	<0.1	1	-		-		<0.1	1
FPSSO	<0.1	3	0.1	1	<0.1	1	-		0.3	19	<0.1	2
FPSSDM	0.2	6	-	-	<0.1	2	-		-		<0.1	0.2
FPSSO2	<0.1	1	-	-	<0.1	1	-		0.2	16	<0.1	2
FPSS	<0.1	1	-	-	-		-		-		-	

[1] FSO fenthion phenol sulfoxide, FPOSODM demethylfenthion oxon sulfoxide, FSO2 fenthion phenol sulfone, FPSSODM demethylfenthion sulfoxide, FPSSO2DM demethylfenthion sulfone, FPOSDM demethylfenthion oxon, FS fenthion phenol, FPSSO fenthion sulfoxide, FPSSDM demethylfenthion, FPSSO2 fenthion sulfone, FPSS fenthion
[2] Flank and loin muscles had similar residues
[3] From samples taken after the first, second and third treatments

Blood levels peaked between 5 and 6½ hours after dosing. Excretion in the urine and faeces was rapid in both pigs with about 85% of the first dose eliminated within 30 hours. After 54 hours the totals

recoverered in the excreta of the male and female pigs were 95% and 91% respectively. Approximately 86-87% of the administered dose was recovered in the urine, 81-84% within the first 24 hours. Faecal elimination accounted for 9% of the total radiolabel in the male and 4% in the female.

Fenthion phenol sulfoxide (35% of the administered dose in the male and 37% in the female) and fenthion phenol sulfone (27% and 18% respectively) were the major products in the urine; fenthion phenol was also present at 11.6% in the male and 5.8% in the female. In the faeces, fenthion and fenthion oxon were the two identifiable compounds, accounting respectively for 4.1% and 1.8% of the administered activity in the male and 1.8% and 0.4% in the female.

Organosoluble material accounted for less than 10% of the total label and most of the radioactivity (72% in the male and 51% in the female) was in conjugated phenols which were identitied after enzymatic hydrolysis.

Total residues in the tissues of the male pig, expressed fenthion, were 8.4 mg/kg kidneys; 8.6 mg/kg liver; 4.7 mg/kg fat; 2.9 mg/kg muscle; 2.4 mg/kg brain and 3.1 mg/kg heart. Residues in the female pig, killed after the longer interval of 30 hours, were substantially lower (1.2 mg/kg kidneys; 0.9 mg/kg liver; 1.6 mg/kg fat; 0.2 mg/kg muscle; 0.2 mg/kg brain; and 0.2 mg/kg heart) indicating effective elimination from the tissues. In the tissues of the male pig fenthion, fenthion oxon, and their sulfoxides and sulfones were found in varying proportions as follows.

Muscle: oxon sulfoxide 47%; oxon sulfone 23%
Heart: oxon sulfoxide 45%; oxon sulfone 26%
Fat: fenthion 16%, fenthion sulfone 30%, oxon sulfoxide 14%; oxon sulfone 22%
Kidneys: oxon sulfoxide 26%; fenthion phenol sulfoxide 14%; fenthion phenol sulfone 12%; fenthion phenol 2%
Liver: fenthion 20%; fenthion sulfone 11%; fenthion oxon 15%; fenthion phenol sulfoxide plus sulfone 10%

Details of the distribution of metabolites in the female animal were not recorded.

The residues in the skin and tissues after dermal treatment were determined in a two-month old pig, approximately 22 kg, given a backline treatment with [1-^{14}C-*phenyl*]fenthion at 14.4 mg/kg bw and killed after 18 hours (Crosby *et al.*, 1990).

The mean ^{14}C levels, as mg/kg fenthion equivalents, were as follows.

Treatment site hair	1400
Treatment site skin	134
Treatment site fat	3.9
Non-treatment site hair	94
Non-treatment site skin	0.4
Non-treatment site fat	0.8
Liver	0.2
Kidneys	0.3
Peritoneal fat	0.6
Muscle	0.1

Extraction efficiencies ranged between 85.9 and 119.2% of the radiocarbon for samples except skin, from which 68.5% was extractable. Total recoveries were between 91.7 and 176.3% (skin 68.9%).

Residues were separated by HPLC and showed the following distribution of identified compounds.

Treatment site	
hair	97% fenthion; 1.7% fenthion sulfoxide
skin	99% fenthion; 0.6% fenthion sulfoxide
fat	100% fenthion
Kidneys	26% fenthion; 6.6% fenthion oxon

Liver	69% fenthion
Muscle	88% fenthion; 12% fenthion sulfoxide
Peritoneal fat	81% fenthion; 11% fenthion sulfoxide

Residues in the kidneys and liver included 67 and 31% respectively of an unidentified metabolite, tentatively thought to be a glucuronide conjugate of fenthion phenol sulfoxide or sulfone (Krautter, 1990b).

Plant metabolism

Data on olives, guavas, cabbage, beans, maize (corn), rice, alfalfa, Bahia grass, Coastal bermuda grass and tea were submitted.

Olives. Two varieties (Leccino and Nocellara del Belice) were given single and double treatments (24-day interval) respectively with 0.5 kg fenthion/ha and olives were picked after 0, 14 and 28 days (Molinari *et al.*, 1992). The residues found in the pulp, oil and pomace after 0 and 28 days are shown in Table 5.

Fenthion and fenthion sulfoxide were the major residue components, with smaller amounts of fenthion sulfone and fenthion oxon.

A half-life of about 11 days was calculated for total fenthion residues under the trial conditions.

Table 5. Distribution of fenthion and its oxidized metabolites in pulp, oil and pomace from olives treated with 1 or 2 applications of fenthion in Italy, 1990 (Molinari, 1992).

Sample	PHI, days	Residue, mg/kg				
		Fenthion	Fenthion oxon	Fenthion sulfoxide	Fenthion sulfone	Total
Leccino variety (single spray)						
Pulp	0	0.62	0.02	0.13	ND	0.76
Oil	0	4.06	1.05	0.10	ND	5.21
Pulp	28	0.11	ND	0.015	ND	0.12
Oil	28	0.50	0.01	ND	ND	0.51
Pomace	28	0.14	0.004	0.07	0.003	0.22
Nocellara del Belice variety (two sprays)						
Pulp	0	1.10	0.04	0.36	ND	1.49
Pulp	28	0.205	0.01	0.04	0.002	0.26
Oil	28	0.93	0.03	ND	ND	0.96
Pomace	28	0.36	0.02	0.26	0.002	0.64

In another series of trials, olive trees were ground-sprayed (with added bait) 3 times (at 8- and 38-day intervals) at approximately 75 g fenthion/ha, or 5 times (at 24-, 8-, 15- and 24-day intervals) at 100 g/ha at a concentration of 0.2 kg ai/hl. Approximately 0.0005 kg fenthion was applied per plant. Samples were taken over a 54-day period after the last sprayings. Residues of fenthion, fenthion oxon and their sulfoxides and sulfones were extracted with chloroform and determined by GLC (Cabras *et al.* 1993).

Fenthion was degraded slowly in both trials with a half-life of about 38 days. Residue levels from 5 treatments were generally higher than from 3. Results are shown in Table 6.

After harvest a 10-kg portion of olives was processed into oil and residues in the oil, oil cake and vegetation water were determined. Details are given in the section "Fate of residues in storage and processing".

Table 6. Residues in olives after treatment with fenthion at 3 x 0.075 or 5 x 0.1 kg ai/ha. Trials were conducted in Italy in 1991 (Cabras *et al.*, 1993).

Compound	Residue, mg/kg, mean ± SD at PHI, days				
	0	11	20	34	54
3 treatments					
Fenthion	0.96 ± 0.28	0.64 ± 0.32	0.51 ± 0.16	0.45 ± 0.18	0.34 ± 0.15
Fenthion sulfoxide	0.66 ± 0.24	0.23 ± 0.08	0.21 ± 0.05	0.20 ± 0.04	0.19 ± 0.08
Fenthion sulfone	0.02 ± 0.00	0.06 ± 0.02	0.05 ± 0.02	0.05 ± 0.01	0.04 ± 0.02
Fenthion oxon	0.02 ± 0.01	0.03 ± 0.01	0.03 ± 0.00	0.02 ± 0.00	0.02 ± 0.00
Fenthion oxon sulfoxide	0.29 ± 0.14	0.25 ± 0.05	0.33 ± 0.06	0.24 ± 0.04	0.07 ± 0.03
Fenthion oxon sulfone	0.03 ± 0.02	0.04 ± 0.00	0.05 ± 0.02	0.03 ± 0.01	not detected
5 treatments					
Fenthion	1.93 ± 0.71	1.43 ± 0.30	1.34 ± 0.31	0.87 ± 0.34	0.72 ± 0.18
Fenthion sulfoxide	0.76 ± 0.22	0.58 ± 0.21	0.56 ± 0.32	0.58 ± 0.26	0.51 ± 0.27
Fenthion sulfone	0.08 ± 0.04	0.15 ± 0.04	0.17 ± 0.06	0.15 ± 0.05	0.12 ± 0.02
Fenthion oxon	0.04 ± 0.01	0.06 ± 0.01	0.09 ± 0.01	0.08 ± 0.01	0.03 ± 0.01
Fenthion oxon sulfoxide	0.34 ± 0.11	0.49 ± 0.06	0.62 ± 0.19	0.80 ± 0.15	0.35 ± 0.09
Fenthion oxon sulfone	0.08 ± 0.05	0.15 ± 0.02	0.18 ± 0.04	0.09 ± 0.02	0.05 ± 0.01

Guavas. A guava tree was sprayed once to run-off with a 0.06% solution of [1-^{14}C-*phenyl*]fenthion (Fredrickson, 1980). Fruit were sampled after 0, 1, 3, 7, 14, 21, 28 and 32 days and the pulp and peel analysed separately.

Most of the ^{14}C remained in the peel (88% at day 0, 78% at day 32). In the peel fenthion (59% of the total activity) and fenthion sulfoxide (26%) were the main residues at day 0. Other metabolites at that time acounted for less than 3% of the total radiolabel. At day 32 the residue included demethylfenthion sulfoxide 52%, fenthion phenol sulfoxide about 12%, fenthion <1%, and fenthion sulfoxide 5.6%.

The radiolabel in the pulp was 1% of the total ^{14}C at day 0, 18% at day 7 and 14% at day 32, with levels of all metabolites <0.1% of the total radiolabel present at day 0. By day 7 the identified residues ranged from 0.1 (fenthion) to 5.4% (demethylfenthion sulfoxide) indicating that some transfer to the pulp had occurred. At day 32, the major pulp metabolite was demethylfenthion sulfoxide (corresponding to 5.5% of the ^{14}C present at that time) with minor amounts of fenthion (<0.1%), fenthion sulfoxide (1%), fenthion sulfone (0.2%), fenthion oxon sulfoxide (1.1%), fenthion phenol (0.4%), fenthion phenol sulfoxide (1.8%), and fenthion phenol sulfone (0.6%),with 3.5% of unextracted ^{14}C. Acid reflux of the unextracted material yielded 40% fenthion phenol sulfoxide, 14% fenthion phenol sulfone, 25% fenthion sulfoxide, and 21% demethylfenthion sulfoxide.

On a whole fruit basis, fenthion and its sulfoxide were the major compounds present shortly after spraying, accounting for 95% of the total ^{14}C. Demethylfenthion sulfoxide was the major compound present at 32 days (60% of the total ^{14}C content) with fenthion phenol sulfoxide (15.7%), fenthion 0.5%, fenthion sulfoxide 8.3%, fenthion sulfone 1.5%, fenthion oxon sulfoxide 6.3%, fenthion phenol 0.6% and fenthion phenol sulfone 3.7%.

Approximately 11% of the applied radiolabel (9.2% as fenthion sulfoxide, 1% as fenthion) could be rinsed off the guavas at day 0. The level of radiolabel in the rinse decreased gradually but erratically to 7.8% of the total ^{14}C at day 32. By day 32, fenthion sulfoxide accounted for about 2% of the total ^{14}C, with similar amounts of fenthion phenol sulfoxide and demethylfenthion sulfoxide.

Cabbage. ^{32}P-labelled fenthion was sprayed onto cabbage plants as a 0.07% water emulsion at the rate of 9 kg fenthion/ha (Tomizawa *et al.*, 1962). The initial concentration of radiolabel in the leaves was 46 mg/kg fenthion equivalents which rapidly diminished over to 3 days to 20% of the original value. Rainfall or evaporation from the leaf surface soon after application were suggested as possible causes of

the loss. The concentration of the radiolabel was relatively constant between 3 and 12 days.

In samples from days 3 to 12, approximately half the labelled material was soluble in chloroform. Fenthion accounted for 95% of the chloroform-soluble radioactivity initially but for less than 1% of it after 7 days. Fenthion sulfoxide and sulfone were not present at day 0 but made up approximately 50% of the total residue at day 7. About 30% of the labelled material present at day 7 was unidentified and may have been hydrolysis products. An identification of the *S*-methyl isomer (iso-fenthion) remains tentative as work by Niessen *et al.*, 1962) showed that the isomer was not formed in beans. The isomer was present as an impurity in the radiolabelled fenthion used by Niessen and it appears that the same material was used in Tomizawa's work.

Beans. Young bean plants were dipped in a 0.2% emulsion containing [^{32}P]fenthion or placed with their roots in an aqueous 0.1% fenthion emulsion (Niessen *et al.*, 1962).

Six hours after the dip treatment most of the radiolabel, about 150 mg/kg fenthion equivalents, was chloroform-soluble and about 20 mg/kg was soluble in water. Over 8 days the chloroform-soluble material decreased to about 15 mg/kg while the water-soluble fraction increased to about 45 mg/kg. Fenthion decreased from about 100 mg/kg at day 0 to about 17 mg/kg after 8 days. Fenthion sulfoxide was the major metabolite identified, with an initial concentration of about 20 mg/kg and a final concentration of about 5 mg/kg, when it made up 52.3% of the residue. Fenthion sulfone and fenthion oxon sulfone and sulfoxide were also detected. The shoots placed in the fenthion emulsion contained about 3 mg/kg of total residue expressed as fenthion, indicative of a slight systemic effect. The *S*-methyl isomer of fenthion was identified as an impurity in the starting material.

Maize. Maize plants (0.08 ha blocks, growth stage not stated) were sprayed once with fenthion (0.5 kg/litre EC) at rates of 560, 1120 or 2240 g fenthion/hectare. Samples were taken at 0, 1, 2, 7, 14, and 21 days after treatment (Leuck and Bowman, 1968). The treated maize plants and maize silage prepared from plants sampled one day after treatment were analysed for fenthion and its oxidized metabolites.

The residue distributions from the three treatments were similar, with levels directly related to the application rates. Fenthion sulfoxide and its oxon were the major metabolites at day 0, with fenthion, its sulfone and oxon sulfone as minor residues. Residues decreased over 21 days when fenthion sulfoxide and sulfone were the main metabolites. Residues of fenthion oxon were not detected (<0.002 mg/kg) in any sample. The dry matter content of the maize was 30-31% initially and 45-53% at day 21. Table 7 summarizes the results.

The analytical method used to determine fenthion and its five metabolites was that of Bowman and Beroza (1968) in which fenthion and the metabolites are extracted with chloroform/methanol, chromatographed on silica gel and determined by GLC with a phosphorus-sensitive flame-photometric detector. Recoveries at the 0.1 mg/kg level were 95-100%, the LOD about 0.003 mg/kg.

Table 7. Fenthion and four of its metabolites in maize plants after a single spraying with fenthion at 0.56, 1.12 or 2.24 kg fenthion/hectare (Leuck and Bowman, 1968).

PHI, days	Rate, kg fenthion/ha	Residues, mg/kg wet weight, mean of four replicates				
		Fenthion	Fenthion sulfone	Fenthion oxon sulfone	Fenthion sulfoxide	Fenthion oxon sulfoxide
0	0.56	0.061	0.07	<0.005	6.02	0.16
	1.12	0.22	0.11	<0.005	9.64	0.30
	2.24	0.41	0.22	<0.005	26.4	0.63
1	0.56	0.036	0.24	0.046	2.76	0.39
	1.12	0.068	0.39	0.054	4.56	0.49
	2.24	0.49	0.52	0.068	16.8	0.75

PHI, days	Rate, kg fenthion/ha	Residues, mg/kg wet weight, mean of four replicates				
		Fenthion	Fenthion sulfone	Fenthion oxon sulfone	Fenthion sulfoxide	Fenthion oxon sulfoxide
2	0.56	0.016	0.24	0.084	2.19	0.45
	1.12	0.041	0.52	0.100	4.36	0.70
	2.24	0.32	0.86	0.130	13.9	0.86
7	0.56	<0.002	0.09	0.090	0.26	0.22
	1.12	0.016	0.44	0.125	0.90	0.47
	2.25	0.039	0.68	0.156	2.38	1.03
14	0.56	<0.002	0.04	0.025	0.073	<0.02
	1.12	0.007	0.14	0.036	0.178	<0.02
	2.24	0.011	0.24	0.085	0.42	0.11
21	0.56	<0.002	0.03	0.019	0.41	<0.02
	1.12	<0.002	0.09	0.020	0.082	<0.02
	2.24	<0.002	0.22	0.036	0.34	<0.02

Maize silage was prepared from day 1 maize plants and dried at 29°C for 30 days. The dry matter in the silage was between 25.8 and 30%. Residues were found to be more persistent in the silage than in the field samples, with a reduced degree of oxidation: fenthion and its sulfoxide and sulfone were the major compounds. Fenthion residues showed an approximatly tenfold increase in concentration in the silage. Residues at 0 and 30 days respectively from the three treatments were as follows.

0.56 kg/ha

Fenthion 0.04, 0.42 mg/kg
Fenthion sulfone 0.24, 0.30 mg/kg
Fenthion oxon <0.002, 0.034 mg/kg
Fenthion oxon sulfone 0.046, 0.031 mg/kg
Fenthion sulfoxide 2.70, 0.93 mg/kg; and
Fenthion oxon sulfoxide 0.39, 0.02 mg/kg.

1.12 kg/ha

Fenthion 0.068, 0.65 mg/kg
Fenthion sulfone 0.39, 0.42 mg/kg
Fenthion oxon <0.002, <0.002 mg/kg
Fenthion oxon sulfone 0.054, 0.010 mg/kg
Fenthion sulfoxide 4.56, 3.11 mg/kg
Fenthion oxon sulfoxide 0.49, 0.16 mg/kg

2.24 kg/ha

Fenthion 0.49, 4.42 mg/kg
Fenthion sulfone 0.52, 0.98 mg/kg
Fenthion oxon <0.002, 0.070 mg/kg
Fenthion oxon sulfone 0.068, 0.025 mg/kg
Fenthion sulfoxide 16.8, 7.0 mg/kg
Fenthion oxon sulfoxide 0.75, 0.21 mg/kg

The total residues (dry weight) at 0 and 30 days were 12.4 and 6.7 mg/kg at 0.56 kg/ha, 18.5 and 15.9 mg/kg at 1.12 kg/ha, and 64.5 and 46.7 mg/kg at 2.24 kg/ha.

Rice. Rice was sprayed with a 0.07% water emulsion of ^{32}P-labelled fenthion at 9 kg/ha at 3 and 5 weeks after transplanting, and also a few days before heading (Fukuda *et al.*, 1962). Whole plants or stems were sampled at various intervals. Ears were sampled at 3, 7, and 12 days after application and grains at 14 and 29 days. Radioactivity was determined by a GM counter.

Most of the radiolabel in transplanted plants was initially chloroform-soluble, with virtually no water-soluble material. By day 7, chloroform-soluble material accounted for <10% of the initial radiolabel. Water-soluble radioactivity never exceeded 10% of the initial label.

After spraying the residues were 121 mg/kg expressed as fenthion on the blade and 28 mg/kg on the sheath from the planats sprayed 3 weeks after transplanting and 153 and 18 mg/kg respectively from spraying after 5 weeks. In the rice sprayed before heading the initial value was 110 mg/kg.

In the plants treated at 3 and 5 weeks fenthion was either absent or accounted for about 10% or less of the chloroform-soluble radiolabel. Chloroform-extractable metabolites were detected throughout the experimental period and consisted mainly of fenthion sulfoxide and sulfone. The *S*-methyl isomer of fenthion was tentatively identified as being present throughout the trials but this compound was present in the starting material as a contaminant at a level of about 3.5%. The metabolic patterns in the sheaths and blades were considered equivalent.

The ears of rice plants sampled 12 days after spraying contained fenthion sulfoxide (45% of the radiolabel) and fenthion sulfone (18%) as the major metabolites. Seventeen per cent of the material present had a TLC R_f value of 0. The *S*-methyl isomer was tentatively identified (19.5% of the ^{32}P).

In rice grains sampled 29 days after spraying, the bulk of the radiolabel was in the bran (60 mg/kg fenthion equivalents). Polished rice had 5.7 mg/kg and husks 2.4 mg/kg. The bran and the polished rice contained 0.9 and 0.1 mg/kg of chloroform-soluble material and 30 and 2 mg/kg of water-soluble material respectively. No chloroform-soluble material was found in the husks, which contained 0.8 mg/kg of water-extractable material.

The water-extractable metabolites in rice grains taken 14 days after application contained phosphoric acid and thionophosphoric acid (approximately 4% of the water extractable material identified); dimethyl hydrogen phosphate (4.5%) dimethyl hydrogen thionophosphate (7%) and demethylfenthion (79%).

Alfalfa. Alfalfa was sprayed with [1-^{13,14}C-*phenyl*]fenthion at a concentration of 0.42 kg fenthion/ha at a plant height of 15-20 cm. (Dräger *et al.*, 1989). Samples were harvested 7 and 30 days after the application. Aueous phase extracts and HPLC fractions were treated with â-glucosidase, cellulase and esterase to release bound metabolites.

Of the applied ^{14}C radioactivity, 65% was in plant material and 8% in the soil. Loss into the air was considered to account for the remainder.

At 7 days there was a total residue of 13 mg/kg expressed as fenthion, which had dropped to 6.6 mg/kg at 30 days. At 7 days approximately 56% of the radioactivity was organosoluble, at 30 days about 30%. Water-soluble radioactivity was about 40% at day 7 and 62% at day 30. About 8% of the radiolabel at day 30 was unextractable.

Extensive metabolism occurred. The identified compounds at days 7 and/or 30 were fenthion, fenthion sulfoxide, fenthion sulfone, fenthion oxon sulfoxide, fenthion phenol, fenthion phenol sulfoxide, fenthion phenol sulfone, demethylfenthion sulfoxide, demethylfenthion sulfone, demethylfenthion oxon sulfoxide and the glucosides of fenthion phenol sulfoxide and sulfone.

Demethylfenthion sulfoxide was a major metabolite throughout. It accounted for about 21% of the recovered ^{14}C after 7 days and 30% after 30 days. Fenthion sulfoxide was initially the major metabolite (41.8% of the radiolabel recovered at 7 days) but it was further metabolized to be 19.7% after 30 days. Fenthion was present at 7 and 30 days but at levels representing less than 2.5% of the total radiolabel recovered at those times. The glucosides of fenthion phenol sulfoxide and sulfone corresponded to 13.9% of the recovered radiocarbon at day 7 and 8.7% at day 30. Fenthion phenols and P=O compounds were present in only trace amounts.

Bahia grass. In an evaluation of the uptake by rotational crops from pastures sprayed with fenthion

(Fredrickson and Thornton, 1978), Bahia grass was sprayed (simulated fog) 4 times at 20-day intervals with [U-^{14}C-*phenyl*]fenthion at about 110 g/ha (the total amount of fenthion applied in the trial was about 450 g/ha).

Grass, soil and water were analysed before and one day after each application. After the grass was harvested (day 126, 66 days after the final application), the sod was turned into the soil and the plot allowed to lie fallow for a year after the initial application. Wheat, sugar beets and spinach were then planted and samples of the growing crops, forage and grain were taken over the respective growing periods.

In the grass, residues increased after each spraying. From a concentration of 8.1 mg/kg fenthion equivalents one day after the first application, the levels had reached 16.1 mg/kg one day after the fourth spraying. After 126 days (66 days after the last treatment), the level in the grass was approximately 0.5 mg/kg.

One day after the initial spray fenthion accounted for 13% and fenthion sulfoxide for 65% of the ^{14}C present, with fenthion sulfone, fenthion phenol sulfoxide and fenthion phenol sulfone each contributing less than 10%. Prior to the third application (day 40) the distribution was fenthion 0.4%, fenthion sulfoxide 20.6%, fenthion sulfone 5%; fenthion phenol sulfoxide 42%; and fenthion phenol sulfone 30%.

One day after the third application fenthion was 2.2% of the residue, fenthion sulfoxide 50.6%, fenthion sulfone 6.4%; fenthion phenol sulfoxide 19.3%; and fenthion phenol sulfone 14.3%. At harvest (day 126) the distribution was fenthion 0.4%, fenthion sulfoxide 2.6%, fenthion sulfone 0.3%; fenthion phenol sulfoxide 62.5%; and fenthion phenol sulfone 27.4%.

Diffuse activity (not associated with any defined TLC R_f value) made up between 2 and 7.8% of the ^{14}C during the 126 days.

The decrease of fenthion sulfoxide with time corresponded to the increasing levels of fenthion phenol sulfoxide and sulfone seen over the same periods.

Samples of the crops grown in the treated soil were taken at regular intervals during their growth and at harvest. Residues were all reported as <0.006 mg/kg fenthion equivalents, the limit of detection, except in dry wheat forage where the value reported was <0.02 mg/kg.

Coastal bermudagrass. Coastal bermudagrass, a forage crop, was sprayed once with fenthion (0.5 kg/litre EC) at a rate of 0.56, 1.12 or 2.24 kg fenthion/hectare and sampled at 0, 1, 2, 7, 14, and 21 days after treatment. The grass was sprayed three weeks after cutting for hay (Leuck and Bowman, 1968). The treated grass was analysed for fenthion and its oxidized metabolites. Fenthion sulfoxide and fenthion sulfone were not present in the starting material.

Residues of fenthion, fenthion sulfoxide and sulfone, and fenthion oxon sulfoxide and sulfone were present at varying concentrations at most sampling intervals. Fenthion oxon was not measurable one day after spraying. Residue concentrations were proportional to the treatment rates.

On the day of treatment fenthion and fenthion sulfoxide were the major components. At 21 days fenthion sulfoxide and fenthion sulfone were the main compounds; fenthion was still present but in low concentrations (<0.1 mg/kg). The dry matter content of the grass was about 50-56% at day 0 and about 42-45% at day 21. Table 8 shows the results.

Table 8. Residues of fenthion and five of its metabolites in Coastal bermudagrass sprayed once with fenthion at 0.056, 0.112 or 0.224 kg/ha and sampled over a 21-day period (Leuck and Bowman, 1968).

PHI, days	Rate, kg ai/ha	Residues mg/kg, wet basis, mean values.					
		Fenthion	Fenthion sulfone	Fenthion oxon	Fenthion oxon sulfone	Fenthion sulfoxide	Fenthion oxon sulfoxide
0	0.56 0.112 0.224	7.67 26.1 64.3	0.47 1.00 0.97	0.007 0.025 0.060	<0.005 <0.005 <0.005	19.1 38.2 71.2	0.33 0.58 1.84
1	0.56 0.112 0.224	0.767 4.56 8.81	1.18 2.27 3.15	<0.002 <0.002 <0.002	0.04 0.069 0.099	14.0 33.0 60.0	1.67 1.18 3.37
2	0.56 0.112 0.224	0.225 1.04 4.54	1.54 3.13 5.04	<0.002 <0.002 <0.002	0.116 0.217 0.198	9.18 23.2 46.4	0.72 1.34 3.46
7	0.56 0.112 0.224	0.056 0.102 0.308	0.99 2.57 4.04	<0.002 <0.002 <0.002	0.133 0.259 0.342	1.77 4.8 10.3	0.38 0.75 1.98
14	0.56 0.112 0.224	0.011 0.032 0.067	0.65 1.74 2.32	<0.002 <0.002 <0.002	0.059 0.141 0.175	0.45 1.07 2.12	0.13 0.23 0.48
21	0.56 0.112 0.224	0.006 0.013 0.034	0.32 0.80 1.30	<0.002 <0.002<0.002	0.033 0.068 0.106	0.15 0.36 0.59	0.02 0.05 0.08

Tea. The fate of [^{32}P]fenthion in tea sprayed at a rate of 9 kg fenthion/ha with a 0.07% emulsion and processed to green tea was reported by Tomizawa *et al.* (1962).

Immediately after spraying levels of ^{32}P (as fenthion equivalents) were 43 mg/kg in younger tea leaves and 90 mg/kg in older leaves. Three days after spraying the level of ^{32}P had dropped to 50-60% of the initial value and continued to decline steadily thereafter.

Fenthion was the only compound identified in both old and new leaves at day 0. It rapidly decreased to less than 1% of the chloroform-soluble ^{32}P present at 7 days. Fenthion sulfoxide and sulfone were the major metabolites from day 3 onwards in both young and old leaves and accounted for approximately 90% of the total ^{32}P at day 7.

In green tea made from the treated leaves, the radioactivity was 59 and 87% of that in fresh leaves taken 3 hours and 7 days after application respectively. The chloroform-extractable metabolites were distributed as follows in fresh leaves, green tea made from leaves taken 3 h after treatment, and green tea made from leaves taken 7 days after treatment respectively. Fenthion sulfoxide: 56.5%, 33.7% and 53%. Fenthion sulfone 30.3%, 56.3% and 23.5%. The residue in the green tea made from "3-hour" leaves also contained 10% of fenthion.

Environmental fate in soil

A rotational crop trial with bahia grass in which residues in soil were determined (Fredrickson and Thornton, 1978) was described above. The composition of the soil used was sand 99%, silt 1%, 2.26% organic matter and pH 6.0.

Levels of radiolabel in the soil were low throughout the study (<0.1 mg/kg fenthion equivalents) and only showed small increases after the sprayings. The concentration was 0.033 mg/kg fenthion equivalents one day after the first spraying and 0.087 mg/kg, the highest residue found, on the day after the second application. When the soil was turned after the four sprayings (126 days after the trial started)

the level was 0.021 mg/kg. After rotational crops had been grown (day 530), the level in the soil was <0.006 mg/kg. Leaching water contained no detectable radioactivity. Characterization of the residues was not possible because of the low levels. When a humic and fulvic acid determination was attempted, the sodium hydroxide extract of a soil sample taken 210 days after the initial application and containing 0.015 mg/kg fenthion equivalents could not be assayed in the liquid scintillation counter because the extract was too dark. Combustion of the remaining solids showed that 20% of the radiolabel was associated with the humin and, by difference, approximately 80% was associated with the humic-fulvic acid fraction.

[1-^{14}C-*phenyl*]fenthion was added to a sandy loam soil (66% sand, 32% silt, 2% clay, 2.4% organic matter, pH 5.1) at 53 mg/kg and exposed to sunlight (Christopher and Lane, 1987a). Fenthion was rapidly degraded (half-life of 6-7 hours) with the formation of fenthion sulfoxide as the major product. After 30 hours fenthion accounted for 34% of the radiocarbon in the sample and fenthion sulfoxide for 58% (2% initially). Fenthion sulfone, fenthion oxon sulfoxide and fenthion phenol sulfoxide were minor products. Quantitative recovery of the radiolabel was achieved with loss through volatility being less than 0.1%. In dark control soil there was little degradation of fenthion over 30 hours (initially 98% of the radiocarbon and after 30 hours 94%). Fenthion sulfoxide accounted for 6% of the radiocarbon at 30 hours.

Fenthion was one of four thioether pesticides (disulfoton, methiocarb and butocarboxim were the others) added to sterile soils (pH 4.5-7.5, clay 8-15%, silt 17-47%, sand 48-70%) at 50-200 mg/kg and exposed to sunlight to investigate their photo-oxidation (Gohre and Miller, 1986). All the pesticides were converted to their sulfoxides with only trace amounts of the sulfone detected. About 45-80% of the originally added material remained after 4 days. The rate of loss was fastest in the least organic soil.

The effect of soil micro-organisms on the degradation of fenthion was studied by Puhl *et al*. (1979). [1-^{14}C-*phenyl*]fenthion was added to non-sterile and sterile loam soil (48% sand, 35% silt, 17% clay, pH 5.5) at 1 mg/kg and aerobically incubated at room temperature (no details provided) for 9 days. Volatile radioactivity was not determined.

Fenthion was degraded more rapidly and extensively in non-sterile than sterile soil. After 9 days fenthion (74% of the total radiocarbon) and fenthion sulfoxide (16%) were the major radioactive species in sterile soil. Fenthion sulfoxide (34%) and fenthion phenol sulfoxide (17%) were the major products in non-sterile soil with lower levels of fenthion sulfone and fenthion phenol sulfone. Fenthion accounted for 12.5% of the total ^{14}C. In the non-sterile soil 72.9% was organosoluble, 15.3% water-soluble and 11% unextracted. In the sterile soil the respective proportions were 95.8%, 2.3% and 1.9%.

The degradation of [1-^{14}C-*phenyl*]fenthion in a silt loam soil (10% sand, 72% silt, 18% clay, pH 5.9) under aerobic and anaerobic conditions has been investigated by Puhl and Hurley (1978a). One or 10 mg/kg of the labelled fenthion was applied to the soil which was then incubated aerobically for 30 days. At this time, several samples treated at 1 mg/kg were flooded with water, the air flushed out with nitrogen and anaerobic conditions maintained for 60 days. Sterilized soil treated at 1 mg/kg was also incubated for 30 days. Light was excluded during the incubations. Aerobic samples at the 1 mg/kg level were sampled over 120 days, and at the 10 mg/kg level over 30 days. Anaerobic samples were taken at 28 and 60 days and sterilized soil samples at 0 to 30 days.

Under aerobic conditions fenthion was rapidly degraded on soil with a half-life of about one day. After 120 days 50% of the radiolabel present was in $^{14}CO_2$, 8% was organosoluble and 42% was unextractable. The products identified, accounting together for <10% of the total ^{14}C, were fenthion sulfoxide and sulfone, fenthion phenol sulfoxide and sulfone, and *O*-methyl fenthion phenol sulfone (3-methyl-4-methylsulfonylanisole), which was the main compound and accounted for 3.8% of the ^{14}C. With 10 mg/kg of fenthion the same compounds were identified in similar proportions over the sampling period of 30 days. The phenol sulfone and carbon dioxide were the main identified products at

30 days.

Under anaerobic conditions degradation was slow with little change in product concentrations between 28 and 60 days, when fenthion phenol sulfone was the major compound. About 42-43% of the radiocarbon was unextractable and 31-34% was due to carbon dioxide.

In the sterile soil, fenthion had a half-life of 14-21 days. Initially it accounted for 94% of the total ^{14}C and its sulfoxide for 4%. After 30 days the proportions were 33% and 34% respectively. Some fenthion phenol sulfoxide appeared towards the end of the trial (less than 10% of the ^{14}C present).

Little radiocarbon was found in aqueous fractions at any time.

The total recoveries of radiocarbon were 98% from 1 mg/kg at 120 days, 102% from 10 mg/kg at 30 days, 89% from anaerobic soil at 60 days, and 120% from sterilized soil at 30 days.

The half-life of fenthion on soils containing 2.6 and 0.6% of organically bound carbon (pH 6.8 and 5.2) was determined over a 10-day period at 22°C (Wagner, 1974, revised 1993). The initial fenthion concentration was 200 ì g/100 g soil. Fenthion disappeared rapidly and less than 10% of the original was present at the end of the study. The calculated half-lives were 1.7 and 0.5 days. Fenthion sulfoxide was the main product.

Mobility

The leaching characteristics of ^{14}C-labelled fenthion and its degradation products on a sandy loam soil (0.6% organic content, 65% sand, 21% silt, 14% clay) under simulated field conditions have been determined (Tweedy and Houseworth, 1974). [1-^{14}C-*phenyl*]fenthion was incorporated into the soil at a rate of 2 mg/10 g of soil and allowed to age for 30 days under greenhouse conditions in an environment protected from light. The soil was then treated for 45 days with water simulating rain- fall and eluates and soil fractions were analysed daily for the radiolabel.

Approximately 4% of the radiolabel was eluted without significant differences in concentration in any of the water samples. About 87% of the applied radiolabel remained in the soil with 67% found in the top 7.5 cm.

In a similar experiment (Simmons, 1975), [U-^{14}C-*phenyl*]fenthion was added to a loam soil at the rate of 10 mg/kg. The treated soil was aged for 30 days at room temperature, then washed for 45 days with water to simulate rainfall. Leachate and soil were analysed for radiolabel content.

Sixteen per cent of the recovered radiolabel was in the leachate and 55% in the top 4 cm of the soil. A 12% loss of radiolabel occurred during the trial. In the leachate only 1% of the activity was fenthion: fenthion phenol, fenthion phenol sulfoxide and fenthion phenol sulfone were identified as major products (10%). Fenthion sulfoxide and sulfone and fenthion oxon were present as minor components.

In a further study of the mobility of fenthion and its breakdown products in soils, [1-$^{13,14}C$-*phenyl*]fenthion was added at 1 mg/kg to a sandy loam soil and incubated aerobically at 22-24°C for 4 or 25 days (Christopher and Lane, 1987b). The aged soil was added to sandy loam, silty clay, silt loam and sand soils (sand 66, 4, 13, and 96%, silt 32, 53, 63 and 2%, clay 2, 43, 24 and 2%, organic matter 2.4%, 2.1%, 2.7% and 0.2% and pH 5.1, 6.7, 6.4 and 6.4). The soils were continuously leached with aqueous calcium chloride solution over a two-day period during which time light was excluded.

Leaching was minimal except from sand, with 95-98% of the radiolabel retained in the soils, mainly in the top 6 cm, and 5% or less in all samples of the leachate. In sand 36% of the radiolabel was

leached from the soil aged for 4 days and 46% from the soil aged for 25 days.

Mineralisation to CO_2 was less than 0.5% of the applied radiolabel during the 4-day aerobic incubation and approximately 7% after 25 days.

In the soils (except sand) fenthion sulfoxide was the major compound after 4 days ageing (29-38% of the radiolabel). Fenthion and its sulfone and fenthion phenol sulfoxide and sulfone were minor components. Fenthion sulfoxide and fenthion phenol sulfoxide and sulfone were the main products after 25 days ageing. In sand aged for 4 days, fenthion sulfoxide was again the major product. After 25 days ageing fenthion, fenthion sulfoxide and sulfone, fenthion phenol sulfoxide, and fenthion phenol sulfone were present in amounts below 10% of the total radiocarbon.

Fenthion was not detected in the leachate from the sand. The compounds identified were fenthion sulfoxide (11% of the radiolabel after 4 days ageing and 0.4% after 25 days, fenthion phenol sulfoxide 9% (4 days) and 15% (25 days); fenthion phenol sulfone 3% (4 days) and 20% (25 days); and fenthion sulfone <1% after both 4 and 25 days.

The mobility of radiolabelled fenthion applied to thin-layer plates coated with different soils was investigated with twenty three other pesticides (Thornton *et al*., 1976). Fenthion was seen to have "low" mobility based on its R_f value (average 0.16) after development of the plates with water. Pesticides of intermediate and greater mobility had R_f values >0.4.

In a study of the mobility and persistence of fenthion in soil and water (Flint and Shaw II, 1972), fenthion spray concentrate (about 11 kg/ha) was added to three soils (loam with 40% sand, 42% silt, 18% clay, 1.4% organic matter, pH 7.7; silty clay loam with 8% sand, 54% silt, 38% clay, 2% organic matter, pH 6.3, and silty clay loam with 6% sand, 54% silt, 40% clay, 4% organic matter, pH 6.1) and the treated soils were leached with water. Run-off water and soils were analysed for residues.

Insignificant leaching was reported, with the majority of the fenthion residues remaining in the top centimetre of the soils. Fenthion residues in the run-off water were less than 1% of the amount applied. Fenthion and fenthion sulfoxide were identified in the soils with only limited migration away from the point of application. Freundlich adsorption constants for fenthion on the three soils were calculated (sandy loam 7.7, silty clay loam 12.4 and high organic silty clay loam 67.3) and showed that adsorption was moderate on sandy soil, a little greater on silty soil and high on soil with a high organic content.

An investigation of the adsorption and desorption of [1-^{14}C-*phenyl*]fenthion added to three soils (Kansas soil 46% sand, 36% silt, 18% clay, pH 5.5; Hagerstown MD soil 4% sand, 53% silt, 43% clay, pH 6.7 and Florida soil 92% sand, 7% silt, 1% clay, pH 6.9) at concentrations of 0.5 to 10.4 mg/kg indicated that fenthion was strongly adsorbed to the soils (Puhl and Hurley, 1978b).

Freundlich adsorption constants were calculated to be between 19 and 39, of the same order of magnitude as those of 7 to 64 determined by Flint and Shaw II (1972) and similar to those determined by Daly (1988). These values were considered high and suggestive of strong soil adsorption coupled with low mobility. The percentage of fenthion adsorbed in all the soils was high (79 to 91%). Less than 15% of the absorbed fenthion was removed after three or four desorptions, a result consistent with the high adsorption.

A further soil adsorption/desorption study with [1-^{13,14}C-*phenyl*]fenthion was conducted on four soils (Daly, 1988). The soil compositions were:

Sand - 88% sand, 7% silt, 5% clay, pH 4.3;
Sandy loam - 56% sand, 30% silt, 14% clay, pH 6.6;
Silt loam - 17% sand, 66% silt, 17% clay, pH 5.9; and

Clay loam - 21% sand, 50% silt, 29% clay and pH 6.4.

The soils were treated with nominal concentrations of 1.0, 5.0, 7.5 and 10 mg/kg and equilibrated with a solution of the radiolabelled fenthion. Adsorption and desorption coefficients were determined with the results shown below.

Soil Type	% organic carbon	Adsorption		Desorption	
		K_d	K_{oc}	K_d	K_{oc}
Sand	0.53	8.62	1638	20.19	3836
Sandy loam	0.58	6.42	1110	12.66	2186
Silt loam	1.53	15.81	1036	33.04	2165
Clay loam	1.16	16.21	1400	28.10	2427

These values confirm that fenthion is resistant to leaching from the soil. The ^{14}C mass balance was between 91 and 104% for the four soils.

Environmental fate in water and sediment systems

Because pesticides may enter natural waters by various routes, e.g. control of aquatic weeds, run-off from agricultural uses, uses against mosquitoes and flies, studies on the fate of fenthion in aquatic situations were reviewed.

The half-lives of fenthion in aqueous phosphate buffers and in a simulated field water system were determined by Flint and Shaw II (1972).

Fenthion (10 mg/kg) was incubated with phosphate buffers at pH 5, 7, and 9 at 30° and 50°C and samples were analysed for fenthion and its degradation products over a period of 16 days. Fenthion had half-lives of 23-31 days at 30°C and 2-6.5 days at 50°C. No sulfoxides, sulfones or oxygen analogues were detected.

In the simulated field water system (pond water, stored outside and exposed to full sunlight), fenthion had a half-life of about 1-1.5 days. The faster degradation in pond water was considered to show the importance of micro-organisms in the aquatic breakdown processes. Fenthion sulfone was identified in silt from the pond water, but was not recorded in the absence of silt. No other products were detected.

A second study on the stability of fenthion in sterile phosphate buffers (Simmons and Thornton, 1976) was conducted by adding 5 mg/kg of the [U-^{14}C-*phenyl*]fenthion to solutions of buffers at pH 5, 7, and 9 and temperatures of 5, 25 and 40°C.

Half-lives of about 70 to 130 weeks were found at all pH values at 5°C with acid solutions being most stable. At higher temperatures the half-lives were much shorter (2-4 weeks at 40°C). The results are shown in Table 9.

Table 9. Half-lives of fenthion in sterile buffer solutions at varying conditions of pH and temperature (Simmons and Thornton, 1976).

pH	Half-lives (weeks) at		
	5°C	25°C	40°C
5	133	8	4
7	105	6	3
9	69	5	2

The effect of temperature on the stability of fenthion is clearly demonstrated, in agreement with the findings of Flint and Shaw II (1972). Fenthion, its sulfoxide and sulfone, fenthion oxon and its sulfoxide and sulfone, fenthion phenol sulfoxide and fenthion phenol sulfone (but not fenthion phenol) were detected. While the relative proportions of these compounds varied with the pH, temperature and time of sampling, fenthion sulfoxide was the principal product and fenthion sulfone a minor constituent. Fenthion oxon was present in varying amounts with maximum values generally associated with higher temperatures and pH and increasing time. Levels of fenthion oxon sulfoxide and sulfone were generally less than 10% of the total ^{14}C and occurred mainly at higher temperature and pH, and longer times. Fenthion phenol sulfoxide and sulfone reached maximum values of about 20 to 36% of the total ^{14}C, also at higher temperatures and pH and longer times.

More than 90% of the radiolabel was initially associated with organosoluble material, which decreased somewhat with time. Less than 10% of the ^{14}C was generally water-soluble except in the 25°C samples where it accounted for 30% at pH 5, 59% at pH 7, and 60% at pH 9 of the total radiolabel present at 10 weeks. As the pH and temperature increased the amount of material not identified (at the origin of TLC plates) also increased with time, most markedly in the 25° and 40°C samples.

In a further investigation of the fate of fenthion in water (Jensen-Korte, 1983a), fenthion at 3.6 to 5.1 ì g/ml was incubated in citrate buffer (pH 4), phosphate buffer (pH 7), and borate buffer (pH 9) at 50, 60 and 70°C. Fenthion concentrations were determined by HPLC and the solutions sampled over times of approximately 30 and 350 hours depending on the buffer system and temperature. The calculated half-lives and those estimated at 22°C by extrapolation are shown in Table 10.

The results confirm that increasing temperature results in faster degradation and show that at 22°C fenthion has a half-life of about 200 days at pH 7. Fenthion phenol was identified in acidic and basic media.

Table 10. Half-lives of fenthion in buffers at pH 4, 7, and 9 at temperatures of 50°C, 70°C, 90°C and, by extrapolation, 22°C (Jensen-Korte,1983a).

pH	°C	Half-life (hours)
4	50	172
4	60	57
4	70	21
7	50	140
7	60	45
7	70	16
9	50	120
9	60	43
9	70	15, 16
4	22[1]	5348
7	22[1]	4792
9	22[1]	3224, 3626

[1] by extrapolation

The fate of fenthion in natural or model aquatic environments, rather than in buffered solutions, was investigated in a number of experiments. Flint and Shaw II (1972, see above) showed

that fenthion in pond water in an outdoor environment was degraded within days.

In a similar situation (Fredrickson, 1976), [U-^{14}C-*phenyl*]fenthion was added at 10 mg/l water to a simulated pond prepared from water and lake silt and stored in the open for a period of 7 weeks. The average daytime temperature over the period was about 20°C.

In the water phase, fenthion was not measurable after 35 days and its half-life was less than 2 days. Fenthion sulfoxide was the major identified degradation product. It was present after one day, reached a maximum of 15% of the ^{14}C content at day 9 and then steadily decreased to 6-7% of the total activity from days 28 to 49. Fenthion phenol was tentatively identified (<2%). Water-soluble activity gradually increased from 2% of the ^{14}C at day 2 to 24% at day 49.

Fenthion was readily transferred to the silt and reached a maximum equivalent to 37% of the ^{14}C present (16 mg/kg) at day 5 and then declined to 9% at day 49. Its half-life in the silt was about 20 days. Fenthion sulfoxide levels were between 1 and 4% of the ^{14}C from day 1 onwards. Low levels (≤2% of the ^{14}C) of residues thought to be fenthion sulfone and fenthion phenol were detected after 16 and 5 days respectively.

Bound activity in the silt gradually increased to a maximum of 46% of the ^{14}C present after 49 days with water-soluble activity being constant at about 2-4% from day 2 onwards.

Twenty-one per cent of the bound activity was extractable and of this 3% was associated with humic acids and 18% with fulvic acids.

The total toxic residues (as parent and its sulfoxide and sulfone) were calculated as having a half-life of 16 days in the total system. The stability of fenthion in silt was attributed to the anaerobic conditions which meant that reduction rather than oxidation predominated. The water-soluble activity was not identified.

An investigation of the degradation of pesticides in an aquatic model system (Scholz *et al.*, 1988) examined, *inter alia*, the effect of oxygen concentration on pesticide breakdown using fenthion as a model. [1-^{14}C-*phenyl*]fenthion was added to water/sediment samples obtained from The Netherlands, Germany, and the USA at a concentration of 1.5 mg fenthion/litre. The systems were kept at 20-24°C under aerobic and anaerobic conditions and sampled over periods of 66 days (aerobic) and 190 days (anaerobic).

In the aerobic system the proportion of water-soluble activity decreased during the trial from 85% to about 5%. About 75% of the ^{14}C at the end of the trial was unextractable and approximately 15-20% had been incorporated into carbon dioxide.

Although radiolabelled carbon dioxide was produced continuously in the aerobic system larger amounts were formed in the anaerobic system after a lag time of 60-120 days, and accounted for about 50% of the radiolabel present at 190 days.

In the aerobic system the major products were fenthion sulfoxide and demethylfenthion oxon sulfone. In the anaerobic system, fenthion phenol sulfoxide and fenthion phenol were the major products, with 3-methylphenol and methane detected as minor constituents. The compounds identified are listed in Table 11.

Table 11. Degradation products of radiolabelled fenthion found in model aquatic systems under aerobic and anaerobic conditions (Scholz *et al.*, 1988).

Aerobic conditions	Both aerobic and anaerobic conditions	Anaerobic conditions

Aerobic conditions	Both aerobic and anaerobic conditions	Anaerobic conditions
Fenthion oxon Fenthion sulfoxide Fenthion oxon sulfoxide Fenthion sulfone Demethyl fenthion sulfone Fenthion oxon sulfone Fenthion phenol sulfone	Demethyl fenthion Demethyl fenthion sulfoxide Fenthion phenol sulfoxide Carbon dioxide	Fenthion phenol 3-Methylphenol Methane

In a study conducted according to the US EPA's guidelines on "Aerobic aquatic metabolism studies", the behaviour and fate of fenthion labelled in the 1-phenyl position with ^{14}C and ^{13}C was investigated (Anderson and Wilmes, 1988). Fenthion (1.5 mg/l) was added to pond water and sediment samples obtained from the USA and The Netherlands. The test systems were open to the atmosphere and maintained with shaking in the dark at 20-24°C. Samples were taken over 66 days. The systems were aerobic throughout the course of the trial.

The mass balances were good, with recoveries of 97 and 106% of the applied radioactivity. While the rates were different, most of the radioactivity in the two systems (56% and 74% of that applied at 66 days) was transferred to the sediment and was not extractable with organic solvents. Carbon dioxide was produced in both systems and accounted for 9.5-12.8% of the final radioactivity.

The degradation of fenthion was rapid in both systems with half-lives of about a week and was accompanied by continuous mineralization. Most of the products were in the aqueous phases, with different compounds predominating at various times: initially fenthion sulfoxide, then demethylfenthion oxon sulfone, and finally fenthion phenol sulfoxide and sulfone. Other compounds identified were fenthion sulfone, fenthion oxon, demethylfenthion, demethylfenthion sulfone, demethylfenthion sulfoxide, and demethylfenthion oxon sulfoxide.

The degradation of fenthion under anaerobic conditions in a simulated aquatic system was also reported by Fritz *et al*. (1988). Water and sediment from a pond were incubated anaerobically in the dark at about 22°C for 360 days with [1-^{14}C-*phenyl*]fenthion added at the rate of 1.5 mg/l.

The initial pH of the surface water was approximately 5.7-5.8, and over the year of the trial steadily increased to 7.2-7.6. Reducing conditions prevailed throughout the system.

The distribution of the radiolabel varied with the incubation period but its rapid appearance in the sediment was noticeable (28% of the applied ^{14}C) after one hour. In water, fenthion decreased from about 72% of the applied radioactivity initially present to about 7% 30 days later and was not detectable after 360 days. In the sediment fenthion was a major component (20% of the applied radioactivity) initially, rose to 60% at 14 days, and then declined to 0.2% at 360 days. Under the anaerobic conditions fenthion was considered to be degraded to methane and carbon dioxide with the system having a first half-life of about 4 to 5 days.

The recovery of radiolabel was >95% up to 60 days and >90% thereafter. The amount of unextracted, bound ^{14}C in the sediment increased irregularly during the trial from 1.5% to approximately 15.6% of the applied ^{14}C. Labelled carbon dioxide was at a maximum at 120 and 190 days when it accounted for about 50% of the applied ^{14}C (in a follow-up experiment). Radiolabelled methane was also detected at these times in the follow-up experiment at about 4% of the total applied radiolabel. No significant amounts of other volatile labelled substances were detected.

Fenthion, fenthion phenol, fenthion phenol sulfoxide, demethylfenthion, demethylfenthion sulfoxide and 3-methylphenol were identified in extracts from the surface water and sediment. Fenthion phenol (maximum values of 30% in the surface water at day 60 and approximately 5% in the

sediment at days 30 and 60) and fenthion phenol sulfoxide (maximum about 24% after 30 days in the surface water and up to 6% in the sediment) were major products at various times. 3-Methylphenol was present at approximately 8.8% and 0.2% in the water at days 60 and 120 and at 0.9% in the sediment at day 60. Only small amounts (<3%) of demethylfenthion and demethylfenthion sulfoxide occurred in the surface water and sediment.

In a model system of salt marsh water and sediment (O'Neill *et al.*, 1989) fenthion was added at a nominal 200 ì g/litre to three microcosms: one sterilized with formalin and without plants, one non-sterile and without plants and one non-sterile with plants. The systems were maintained in light and darkness at 20°C. Water samples were taken during the following 190 hours, and leaves and sediment were analysed for fenthion at the end of the experiments. The results were used in the validation of a computer modelling system.

Fenthion loss from the water followed first order kinetics with levels of fenthion in the non-sterile systems approaching zero by 200 hours. In the sterile system fenthion was still present in the water after 200 hours at a level between 50 and 100 ì g/litre.

Half-lives were estimated to be about 4 days in the sterile system and about 33-35 hours in the two non-sterile systems.

The fate of 28 pesticides, including fenthion, in river water has been reported (Eichelberger and Lichtenberg, 1971). Fenthion was added to river water at the rate of 10 ì g/l and kept for a period of 8 weeks under laboratory conditions in natural and artificial light. Within one week, 50% of the original fenthion was left, at 2 weeks 10% was present and none was detected after 4 weeks. In similarly treated distilled water no fenthion was lost over a three-week period, an indication of the role of biological activity in the degradation of fenthion.

The photolysis of fenthion in distilled water has been investigated by Fredrickson and Nichols (1976). Distilled water containing [U-^{14}C-*phenyl*]fenthion at 5 mg/l was irradiated with artificial light sources approximating the spectral wavelengths of sunlight. The water temperatures were 5°C and 25°C. The effect of acetone as a photosensitizer mimicking the sensitizing effects of dissolved substances in natural water was also investigated at 25°C. Irradiation was for 120 minutes at 25°C and 160 minutes at 5°C.

Rapid breakdown of fenthion was observed in all situations with the half-lives at 5°C and 25°C of 55 and 15 minutes respectively. In the presence of acetone the half-life was 10 minutes. The degradation products identified were fenthion sulfoxide and sulfone, fenthion oxon and its sulfoxide, and fenthion phenol and its sulfoxide and sulfone. At 25°C, the major compounds at 120 minutes were fenthion sulfoxide (18% of the activity) fenthion oxon sulfoxide (15%) and fenthion phenol sulfoxide (12%). Thirty-nine per cent of the ^{14}C present was associated with unidentified polar metabolites, believed to be polymeric in nature with a high molecular weight (>700).

At 5°C after 160 minutes fenthion (22%), fenthion sulfoxide (12%), fenthion oxon (13%), fenthion phenol (17%), and fenthion phenol sulfoxide (12%) were the major compounds. Polar material accounted for 26% of the activity at that time.

In the sensitized solution after 120 minutes, fenthion sulfoxide (35%) and fenthion phenol sulfoxide (12%) were the main identified compounds, with 36% of polar degradation products.

Irradiation of a 3.5 mg/l solution of fenthion in distilled water for 10 minutes with a high-pressure mercury vapour lamp showed a half-life of 4.5 minutes for fenthion (Jensen-Korte, 1983b). In the same study a solution of fenthion in distilled water exposed to summer sunlight had a half-life

of four hours. A large number of photoproducts were formed, with the positive identification of fenthion sulfoxide and fenthion phenol.

The photolysis of fenthion at pH 5 in sterile sodium acetate buffer was studied with [1-^{13,14}C-*phenyl*]fenthion at a concentration of 7 mg/l (Christopher and Lane, 1987c). Photolysis was by a light source stated to have had a similar spectral distribution to natural sunlight. Irradiation was over a 4-hour period and dark controls were run to check that the products formed were from photochemical processes only. The control solutions contained only fenthion (average 94%) and fenthion sulfoxide (average 3%).

Throughout the irradiation, the buffer temperature was 22-24°C. Recoveries of radioactivity were between 79 and 103%. A half-life of about 30 minutes was calculated, with extensive degradation of the fenthion.

Fenthion phenol, fenthion sulfoxide, fenthion phenol sulfoxide and fenthion phenol sulfonic acid were major photoproducts. Other photoproducts identified included fenthion sulfone and fenthion oxon sulfone. The radioactivity recovered from the HPLC column in these determinations averaged 90% of that injected.

Organosoluble material accounted for 99.8% of the recovered radiocarbon at time 0 and 87.4% at 4 hours, and water-soluble material for 0.2% and 12.6% respectively.

In a study to investigate the direct photodegradation of organic compounds in water under environmental conditions (Wilmes, 1988), fenthion was reported to have had experimental half-lives of 4 hours in the summer and 11 hours in the autumn compared to half-lives of 3 hours in summer and 14 hours in autumn calculated on the basis of the quantum yield of photodegradation in water in monochromatic or polychromatic light.

METHODS OF RESIDUE ANALYSIS

Methods to determine fenthion and its oxidative metabolites in animal tissues, milk and plant materials were presented. Earlier methods measured total phosphorus, but fenthion and its intact metabolites are now determined by GLC either individually or collectively as fenthion oxon sulfone. The earlier GLC methods required a hydrolysis step to form the fenthion phenols which were brominated and acetylated before determination. This approach was simplified by the omission of the hydrolysis and derivatization steps and the substitution of oxidation to fenthion oxon sulfone which is determined by GLC with appropriate detectors. Fenthion and its metabolites have also been determined by HPLC.

Clean-up

Permeation chromatography on a polystyrene gel is used to clean up animal and plant extracts for pesticide determination in the DFG method (Thier and Kirchoff (Ed), 1992). Chromatography is on Bio-Beads S-X3 with equal volumes of cyclohexane and ethyl acetate as eluant. Fenthion, fenthion sulfone, fenthion sulfoxide, fenthion oxon sulfoxide and fenthion oxon sulfone are separated and can be individually determined.

General analytical methods

Fruits and vegetables. The extraction process of Frehse *et al.* for olives (1962a) was developed for plant material in general (Frehse *et al*., 1962b). The material was extracted with acetone, the extract filtered and the acetone evaporated. The aqueous residue was extracted with chloroform and the

chloroform evaporated. The resulting residue was dissolved in petroleum ether, extracted with ethanol, and further cleaned up by chromatography on aluminium oxide and activated carbon columns.

Potassium permanganate was used to oxidize fenthion residues to fenthion sulfone and oxon residues to fenthion oxon sulfone. Fenthion sulfone was determined by infra-red spectroscopy using the sulfone band at 1325 cm^{-1}. Phosphorus determination by wet ashing and the formation of phosphomolybdenum blue could be used to confirm the result. Limits of detection were stated to be 0.01 mg/kg for cherries, 0.03 mg/kg for beets, 0.06 mg/kg for beet leaves, and 0.07 mg/kg for apples and cole crops. Blank values of 0.7-0.8 mg/kg were found on occasion in leaves. Using ^{32}P-labelled fenthion, recoveries were about 77-83%. In 1984 recoveries using this method were 40-50% from guavas, 75% from olives and olive oil, and 80% from peas (fortification levels not stated). Recoveries from grapes were 130% at 0.23 mg/kg, 80% at 0.45 mg/kg, 70% at 0.9 mg/kg, and 65% at 1.8 mg/kg (Wagner, 1984).

Fenthion was extracted by a simpler process developed for the pesticide disulfoton in crops with lower chlorophyll content, e.g. potatoes or apples (Niessen and Frehse, 1969a,b). The plant material was macerated with acetone, and the filtered solution mixed with water and extracted with chloroform. The residue from the chloroform extract was dissolved in chloroform/carbon tetrachloride (1:1 v/v), cleaned up on an alumina column and determined colorimetrically as total phosphorus. The method was non-specific and identification of the metabolites was by paper chromatography. Details of recoveries were not provided.

Residues of organophosphorus pesticides containing thioether groups when present as the parent compounds and/or sulfoxides and sulfones were determined in fruits and vegetables as the sulfone by Thier and Zeumer (1987). Residues were extracted with acetonitrile, co-extracted water was removed by the addition of dichloromethane, the solvent was evaporated and the residue dissolved in acetone. Fenthion and fenthion sulfoxide were oxidized to fenthion sulfone with potassium permanganate. This step removed most of the interfering plant material and column clean-up was not routinely needed. The residue was extracted into dichloromethane and determined by gas chromatography on a packed column with a phosphorus-specific alkali flame ionisation detector. Recoveries from apples and cherries at the 0.1 mg/kg level were ≤85% and in a variety of vegetables at the same level also acceptable (>70%). At lower levels (0.05 and 0.01 mg/kg) recoveries were >70% in most cases. Recoveries from leeks were 66% at 0.01 mg/kg. Recoveries of the oxon were not reported. Recoveries of fenthion sulfoxide and sulfone from carrots and spinach at 0.1 mg/kg were 90-95%. Individual determinations of the parent, sulfoxide and sulfone were possible if the oxidation step was omitted.

In the regulatory method of The Netherlands (Ministry of Welfare, 1988a) fenthion residues are extracted from agricultural products with ethyl acetate in the presence of sodium sulfate. The filtered extract is analysed without further clean-up by gas chromatography with phosphorus-specific detection. Limits of determination are 0.01-0.05 mg/kg, with recoveries of >80%. The method measures fenthion only.

Fenthion residues in fruiting vegetables and subtropical and tropical fruits were determined after post-harvest disinfestation with fenthion (Jorgensen *et al.*, 1995). The sample was macerated with acetone and filtered. Water was added and the acetone evaporated. The aqueous phase was extracted with hexane which was dried over sodium sulfate, reduced to 2 ml, and cleaned up by sweep co-distillation. The resulting hexane solution was analysed for fenthion by GLC using a flame-photometric detector. This method was suitable for capsicum peppers, mangoes, tomatoes and zucchini. Cucumbers and rockmelons did not require the sweep co-distillation clean-up. The limits of determination were 0.01-0.02 mg/kg with the following recoveries: capsicums 83% at 0.2 mg/kg; cucumbers 91% at 0.6 mg/kg and 88% at 1.1 mg/kg; mango pulp 97% at 0.1 mg/kg; mango peel 83%

at 0.7 mg/kg; rockmelon 91% at 0.6 mg/kg and 99% at 1.2 mg/kg; tomatoes 83% at 0.9 mg/kg: zucchini 87% at 0.5 mg/kg.

Animal products. A method to determine fenthion and its unhydrolysed metabolites in animal tissues was reported in the mid-1960s (Anderson and Katague, 1965). The sample was successively extracted with acetone and chloroform. After evaporation of the combined solvents, the residue was partitioned between n-hexane and acetonitrile. The acetonitrile was evaporated and the fenthion residues oxidized with *m*-chloroperbenzoic acid to fenthion oxon sulfone. Hydrochloric acid was used to extract the sulfone which was in turn extracted into chloroform. After washing with an alkaline solution, the chloroform was evaporated and the resulting residue hydrolysed with sodium hydroxide. The phenol formed was extracted from the acidified solution with chloroform, then brominated and acetylated and determined by gas chromatography with an electron-capture detector. The LOD was 0.1 mg/kg. Satisfactory recoveries (means of 71-108%) were generally reported for fenthion, fenthion oxon sulfoxide and fenthion oxon sulfone from cattle brain, fat, heart, kidneys, liver, and muscle after spiking at 0.1 mg/kg. The report noted that owing to the complexity of the process and the number of reactions, results for standards varied by ±20% and a standard had to be included with each set of samples. In a published version of the method (Anderson *et al.*, 1966) it was stated the inherent sensitivity was better than 0.1 mg/kg. Details of the recoveries of fenthion, its oxon sulfoxide, and its oxon sulfone following some small modifications to the method were provided (Chemagro, 1965e). At 0.01 mg/kg, recoveries were 89-114% for fenthion and the oxon sulfoxide, and 93-105% for the oxon sulfone. Control values were <0.0025 mg/kg (average 0.001 mg/kg).

A modification of the alkaline washing of the chloroform extract obtained after the *m*-chloroperbenzoic acid oxidation step, combined with a lower loading of the chromatographic column, improved the sensitivity and resolution of the method (Katague, 1966). This allowed determination of fenthion and its oxon sulfoxide and sulfone in milk at the 0.01 mg/kg level. Reported average recoveries of fenthion and its oxon sulfoxide and sulfone from animal tissues at 0.1 mg/kg were between 71 and 108%.

In a further development of the Anderson and Katague method, the hydrolysis and derivatization steps were omitted and the fenthion oxon sulfone was determined directly (Thornton, 1967). After the *m*-chloroperbenzoic acid oxidation the oxon sulfone was extracted successively with acid and chloroform, and the chloroform evaporated from the washed extract as before. The residue was dissolved in acetone and determined by gas chromatography with thermionic detection. The LOD was 0.05 mg/kg. Recoveries of fenthion and its oxon sulfoxide and sulfone from cattle brain, heart, kidneys, and muscle were more than 80% at 0.1 mg/kg, but that of fenthion from bovine liver was only 64%. Recoveries of the three compounds from chicken giblets and muscle were in the range 87 to 118% at 0.1 mg/kg. Forty-two other organophosphorus pesticides registered in the USA for use on meat, fish and poultry at that time were stated not to have interfered with the determination when they were added at the 5 mg/kg level.

In the regulatory method used for veterinary products in The Netherlands fenthion residues are extracted with acetone/acetonitrile, with the addition of filter aid. The filtered extract is evaporated to dryness and the residue dissolved in hexane/acetonitrile. Fenthion is determined by gas chromatography with phosphorus-specific detection. The LOD is 0.01-0.04 mg/kg, with recoveries of 66-102%. The method determines only fenthion (Ministry of Welfare, 1988b).

The Netherlands also uses a qualitative TLC method to detect fenthion residues (Ministry of Welfare, 1988c) after extraction with ethyl acetate in the presence of sodium sulfate. An aliquot is applied to a TLC plate and the developed plate is sprayed with a bromine solution, then with a homogenate of bee heads. After incubation at 37°C, the plate is sprayed with 2-naphthyl acetate and Fast Bleu B. The cholinesterase from the bee heads hydrolyses the acetate to 2-naphthol which causes a coloured dye to form. If fenthion is present, the reaction cannot occur and a white spot is seen on a

pink-violet background.

The separate determination of fenthion and fenthion sulfone residues in sheep liver, kidneys, muscle and subcutaneous fat has been reported by Cameron *et al.* (1995). The sample is macerated with acetonitrile and the decanted acetonitrile shaken with hydrochloric acid solution and hexane. The hexane layer, containing the fenthion, is partitioned with hexane-saturated acetonitrile and the acetonitrile phase evaporated. The residue is redissolved in hexane, cleaned up on a silica Mega Bond Elut cartridge eluted with acetone/hexane, and the solvent evaporated. The residue is dissolved in acetonitrile/water for HPLC determination. The original acid aqueous layer is partitioned with dichloromethane and the dichloromethane evaporated. The residue, containing the sulfone, is cleaned up and transferred to acetonitrile/water for HPLC determination as before. Fenthion is measured at 253 nm and fenthion sulfone at 205 nm. The LOD was 0.02 mg/kg for both fenthion and the sulfone, and the limit of detection 0.005 mg/kg.

Fenthion recoveries from muscle and subcutaneous fat at 0.1 mg/kg were 68.7 and 73.2% respectively, and from liver, kidneys, muscle, and subcutaneous fat at 0.04 mg/kg 60-96.4%, 60.8-89.2%, 68.2-89.8%, and 68.5-84%.

Recoveries of fenthion sulfone from liver, muscle and subcutaneous fat at 0.1 mg/kg were 86.5, 79.6 and 83.1% respectively, and from liver, kidneys, muscle, and subcutaneous fat at 0.04 mg/kg 76.5-89%, 76.9-110%, 74.5-85.7%, and 67.8-82.8%.

A method for eggs and milk (Olson, 1968) is essentially identical to that of Thornton (1967, see above). Fenthion and its metabolites are oxidized to the oxon sulfone which is determined by GLC with an AFID.

The LOD was 0.005 mg/kg. Recoveries from milk and eggs of fenthion, its oxon sulfoxide and its oxon sulfone at 0.01 and 0.005 mg/kg were between 74 and 128%.

Specific methods

Rice. Olson (1967) used *m*-chloroperbenzoic acid to oxidize fenthion and its metabolites to the oxon sulfone to determine fenthion residues in rice.

After blending the sample with acetone, chloroform was added to the filtered solution and the water which separated discarded. The organic phase was evaporated and the residue oxidized with *m*-chloroperbenzoic acid. The oxidized mixture was extracted with hydrochloric acid and the fenthion oxon sulfone extracted into chloroform. After evaporation of the chloroform, the residue was dissolved in acetone and the sulfone determined by gas chromatography, using a packed column and a phosphorus-sensitive detector. Recoveries at 0.1 mg/kg of fenthion and its oxon sulfoxide and sulfone were 75% or higher. The LOD was 0.05 or lower. The results were confirmed by the use of a column with a more polar phase.

A TLC clean-up procedure was used to determine fenthion residues in harvested rice grains by Takase *et al.* (1971). The sample was extracted with benzene, cleaned up by TLC on alumina and the residues determined by GLC with a flame-photometric detector. The limit of detection for fenthion was 0.001 mg/kg with a recovery of 97% at 0.1 mg/kg. The LOD was stated to be 0.005 mg/kg or better.

Total residues of fenthion in rice grain were determined by GLC as fenthion sulfone and fenthion oxon sulfone after oxidation with potassium permanganate (Takino and Kurogochi, 1995). The method determined the sum of fenthion and its sulfoxide and sulfone (total thiono compounds, total P=S) and the sum of fenthion oxon and its sulfoxide and sulfone (total oxons, total P=O).

Omission of the oxidation step allowed the determination of fenthion. Samples were extracted with acetone and the acetone extract partitioned with dichloromethane. The dichloromethane phase was evaporated and the residue partitioned between n-hexane and acetonitrile. The acetonitrile phase was evaporated and the residue dissolved in dichloromethane. An aliquot was cleaned up by Florisil column chromatography and fenthion determined by GLC with a flame-photometric detector. The residue left after evaporation of a second aliquot was dissolved in acetone and oxidized with aqueous potassium permanganate. The sulfones formed were partitioned into dichloromethane. The solvent was evaporated, and the residue dissolved in acetone and analysed for fenthion sulfone and oxon sulfone by GLC with a flame-photometric detector. The limits of detection were 0.005 mg/kg for all three determinations.

When untreated rice grains were fortified with fenthion and 5 metabolites at a level of 0.1 mg/kg recoveries through the complete method including the potassium permanganate oxidation step were fenthion 88%, 90%; fenthion sulfoxide 105%, 106%; fenthion sulfone 95%, 98%; fenthion oxon 99%, 100%; fenthion oxon sulfoxide 96%, 100%; fenthion oxon sulfone 88%, 90%. Then fenthion alone was determined at the same level without the oxidation step the recovery was 103%.

Citrus fruit and peel. A modification of the method of Olson (1967) for rice gave recoveries at a 0.1 mg/kg fortification level of 86% from the fruit and 106% from the peel (Wagner, 1982).

Orange (including peel and marmalade). Fenthion residues were determined as the oxon sulfone by a development of the method of Olson (1967) for rice (Ohs, 1991a). The limit of determination was stated to be 0.01 mg/kg and recoveries at that level were 70 and 73% from fruit and 96% from juice. In a later modification (Ohs, 1991b) orange peel was macerated with an acetone/water mixture and filtered. A portion of the filtrate was evaporated and the aqueous residue extracted with dichloromethane before oxidation. Recoveries at 0.01 mg/kg were reported as 70 and 70%. Using the same modification recoveries from orange marmalade were stated to be between 80 and 121%.

Apples, pears. Residues of fenthion were determined as fenthion oxon sulfone in apples, apple juice, purée and pomace, pears and pear preserve by a development of the method of Olson (1967) for rice (Ohs, 1990, 1991b).

Apples were macerated with acetone, the macerate mixed with water and filtered. A portion of the filtrate was extracted with dichloromethane. The extract was dried with sodium sulfate and concentrated to dryness. In a later modification (Ohs, 1991b) apple pomace was macerated with an acetone/water solution and filtered. A portion of the filtrate was evaporated and the aqueous residue extracted with dichloromethane as for apples. After oxidation with *m*-chloroperbenzoic acid the reaction mixture was added to isopropyl ether and thoroughly extracted with hydrochloric acid solution. The acid solution was extracted with dichloromethane, which was dried over sodium sulfate and evaporated. The residue was dissolved in ethyl acetate and analysed by gas chromatography on a megabore column with a flame-photometric detector optimised for phosphorus.

Apple juice was applied to a Chem-Elut cartridge and allowed to react for several minutes before elution with dichloromethane, evaporation of the solvent, and oxidation with *m*-chloroperbenzoic acid.

The limit of determination was stated to be 0.01 mg/kg with the following recoveries.

Apples	90 and 94% at 0.01 mg/kg 73 and 74% at 0.5 mg/kg
Apple purée	78 and 86% at 0.01 mg/kg
Apple juice	84% at 0.01 mg/kg
Apple pomace	79 and 84% (Ohs, 1990)

	93-124% at 0.01 mg/kg (Ohs, 1991b).
Pears	65 and 75% at 0.01 mg/kg
	84 and 87% at 0.5 mg/kg
Pear preserve	86 and 89% at 0.01 mg/kg
	123 and 126% at 0.5 mg/kg

Cherries, peaches. The procedue used for apples and pears was extended to cherries (Wagner, 1985) and peaches (Ohs, 1994a). The limit of determination for cherries was stated to be 0.05 mg/kg with a 78% recovery at 0.1 mg/kg.

Recoveries from peaches fortified with fenthion, its oxon, and their sulfoxides and sulfones were 76-86% at 0.01 mg/kg, 74-81% at 0.1 mg/kg, and 74-87% at 0.5 mg/kg. The limit of determination was 0.01 mg/kg.

Olives and olive oil. A colorimetric method for fenthion and its metabolites in olives and olive oil (Frehse *et al*., 1962a) depended upon the determination of phosphorus after wet-ashing. It required extensive clean-up and was non-specific. The lower limits of detection were reported as 0.05 mg/kg for olives and 0.1 mg/kg for olive oil. Recoveries of 75-80%, using ^{32}P-labelled mixtures of fenthion and its metabolites were reported.

A modification of the methods of Olson for the determination of fenthion residues in rice (1967) and eggs and milk (1968) as fenthion oxon sulfone was applied to olive oil and olives by Wagner (1979). Olive oil was extracted with acetonitrile and the residue left after evaporation of the solvent dissolved in petroleum ether. The petroleum ether was shaken with acetonitrile and the acetonitrile phase washed with petroleum ether. The oily residue left after evaporation of the acetonitrile was oxidized to fenthion oxon sulfone according to the method of Olson. Quantification was by gas chromatography. Olives were macerated with petroleum ether in the presence of sodium sulfate. After filtration and removal of the solvent the residue was worked up in the same way as olive oil. Recoveries at 0.1 mg/kg were 74% from olives and 94% from the oil.

Residues of fenthion and its oxidized metabolites in olive oil were determined after oxidation with potassium permanganate to fenthion sulfone or oxon sulfone (Lentza-Rizos and Avramides, 1990).

The oil was mixed with hexane saturated with acetonitrile, 1 ml of deionised water was added and the mixture shaken. The acetonitrile layer was mixed with more hexane saturated with acetonitrile and the extraction procedure repeated twice using 1 and 0.5 ml of water. The acetonitrile was evaporated from the combined extracts, the residue dissolved in acetone, and potassium permanganate solution added. The reaction mixture was extracted with dichloromethane, which was then evaporated and the residue dissolved in acetone. Fenthion sulfone and its oxon were determined by gas chromatography on a packed column with a nitrogen-phosphorus detector.

Fenthion recoveries were highest (>99%) when the volumes of added water were small and only if the water was added after the initial mixing with the hexane and acetonitrile. Recoveries of fenthion, its sulfoxide, sulfone and oxon sulfone from the extraction step at 0.1 and 1 mg/kg fortification levels were all greater than 99%. Fenthion oxon and its sulfoxide were not determined because standards were not available but it was noted in the report that the total concentration of P=O metabolites was an insignificant part of the residues in olive oil. For the whole method, recoveries of standards and from oils were >79%. Limits of determination were 0.005 mg/kg for fenthion sulfone and 0.01 mg/kg for the oxon sulfone. Potassium permanganate was chosen as an oxidant because it left the P=S bond intact. The recovery of the fenthion oxon sulfone was high on occasion, reaching 147% from a 1 mg/kg standard and 198% from an oil at 0.1 mg/kg.

fenthion

Residues of fenthion, its sulfoxide, sulfone and oxon in olives, olive paste and olive pulp were determined without prior oxidation (Molinari and Fontana, 1992). Olives (pitted or unpitted) were homogenised with acetonitrile, the filtered acetonitrile extract dried on a sodium sulfate column and then extracted with n-hexane saturated with acetonitrile. The acetonitrile was evaporated and the residue dissolved in acetone and cleaned up on an alumina column with ethyl acetate as eluant. After removal of the solvents, the residue was dissolved in ethyl acetate and analysed by gas chromatography on a capillary column with a nitrogen-phosphorus detector with parathion-methyl as an internal standard. The aqueous phase from the original acetonitrile extraction was extracted with methylene chloride and that extract then treated in the same way as the acetonitrile extract. Olive oil was analysed directly after dilution with ethyl acetate. Recoveries were stated to be about 80% with detection limits of 5 to 10 ì g/kg for fenthion and the metabolites.

A development of the method of Olson (1967) for rice was applied to the determination of fenthion residues as the oxon sulfone in olives and olive oil (Olson, 1988; Ohs, 1991b). The methods are essentially those of Ohs (19990, 1991b) for apples and pears.

Olives were extracted by two procedures. In the 1988 work they were homogenised with acetonitrile and filtered and the aqueous remainder, after evaporation of the solvent, extracted with dichloromethane. The dichloromethane was dried with sodium sulfate and evaporated. The residue was taken up in petroleum ether and partitioned into acetonitrile. The residue left after evaporation of the acetonitrile was then oxidized. In the 1991 work, the olives were first shaken and then homogenised with acetone/water, the acetone was evaporated and the aqueous remainder extracted with dichloromethane. After drying with sodium sulfate the solvent was removed and the residue partitioned between acetonitrile and hexane. The acetonitrile phase was concentrated and the residue oxidized according to the method of Olson. Olive oil was extracted in both procedures with acetonitrile and the acetonitrile phase shaken with petroleum ether. After evaporation of the acetonitrile, the residue was oxidized as before. Determination was by GLC on a magabore column with flame-photometric detection.

Recoveries in the 1988 work from olives were 81% at 0.01 mg/kg and 83% at 0.1 mg/kg, and from olive oil 86% at 0.01 mg/kg and 81% at 0.1 mg/kg. The lower practical limit of determination was 0.01 mg/kg. In the 1991 work the recoveries from olives were 73-82% at 1.0 mg/kg and from olive oil 81-85% at 0.01 mg/kg. The limit of determination was 0.01 mg/kg.

Soil. Soil was mixed with water and then macerated with acetone. The macerate was filtered and the filtrate extracted with dichloromethane. The extract was dried with sodium sulfate and concentrated to dryness before oxidation with *m*-chloroperbenzoic acid. The residue was determined by gas chromatography. The limit of determination was stated to be 0.05 mg/kg with a 90% recovery at the 0.5 mg/kg level (Wagner, 1985).

Water. Wagner (1985) determined fenthion residues in leachate water, after direct extraction with dichloromethane, by the procedure described for soil. The limit of determination was 0.05 mg/kg with 80% recovery at 0.5 mg/kg.

Fenthion residues were determined in drinking water by the method used for appled juice (Ohs, 1990). The limit of determination was 0.01 mg/kg with recoveries of 90 and 94% at that level.

Fenthion was determined in water by TLC after solid-phase extraction on alkyl-modified silica gel (Burger, 1988). The extract was desorbed with acetonitrile/methanol and the residues determined by gradient elution on HPTLC silica gel plates with detection by derivatization and UV and quantification by comparison with external and internal standards. The method was suitable for a number of classes of pesticides and had a limit of determination of 0.05 ì g active ingredient/litre. Recoveries of fenthion at a fortification level of 0.1 ì g/l were in the range 59-69%. A modification

using dichloromethane for elution of the solid-phase extract gave recoveries of 68-93% at 0.05 ì g/l (Burger, 1990). No reference was made to the determination of fenthion oxidation products.

Stability of pesticide residues in stored analytical samples

Olives and olive oil. Olives and olive oil fortified at 0.2 mg/kg with fenthion, its sulfoxide and sulfone and fenthion oxon sulfoxide and sulfone were stored below -20°C for 380 days. The total level of fenthion and the metabolites was equivalent to 1 mg/kg (Ohs, 1993).

Olives were extracted with acetone or acetone/water and olive oil with acetonitrile. Residues were determined according to Ohs (1991b). At intervals the stored samples and freshly prepared spiked samples were analysed and the results compared. Residues in stored olives and oil were respectively 83-115% and 101-114% of those in the freshly spiked samples. The results are shown in Table 12.

Table 12. Stability of fenthion residues in frozen olives and olive oil.

Olives			Oil		
Day	Residues, found/added, %		Day	Residues, found/added, %	
	Stored	Fresh		Stored	Fresh
0	79.0	83.6	0	90.4	88.1
7	65.5	54.0[1]	6	87.1	82.8
13	75.0	85.2	12	95.2	89.5
27	83.9	89.8	26	96.9	88.3
71	62.0	61.2[1]	70	84.9	83.7
91	80.6	72.3	89	88.1	84.9
182	68.8	79.7	181	92.6	81.2
335	77.4	93.5	334	92.6	90.2
380	81.3	70.6	379	86.6	81.0

[1] Although these recoveries were below 70%, they were not reanalysed because of the relatively short time between these and the next storage intervals

The results show that fenthion, its sulfoxide and sulfone and fenthion oxon sulfoxide and sulfone were stable in olives and olive oil when stored at -20°C for 380 days.

Lentza-Rizos and Avramides (1994) stored refined olive oil fortified with 1 mg/kg fenthion at -22 to -18°C and with 2 mg/kg at 17-23°C for a year. The samples were stored in brown bottles. Additional samples of virgin olive oils containing incurred fenthion residues of ≥0.5 mg/kg taken during monitoring studies were stored in brown bottles at 17 to 23°C and analysed at various intervals between 1 and 11 months.

Samples were extracted by partitioning between petroleum ether and acetonitrile with water. Fenthion and its sulfoxide were determined by gas chromatography on a packed column with a nitrogen-phosphorus detector. Fenthion sulfone and the three oxons were not determined, since it had been concluded that fenthion sulfoxide was the only metabolite of significance in stored olive oil.

The total fenthion residues were stable in both sets of fortified sample over a year of storage. In the samples with incurred residues there was no decrease in the total residue, but a slow conversion of fenthion to fenthion sulfoxide was reported.

The results show that total fenthion residues were stable for a year of storage at both -22 to -18°C and at 17-23°C.

Orange peel and pulp. The stability of fenthion residues in orange peel and pulp during frozen storage has been reported by Ohs (1993). The peel and pulp were each fortified at 0.2 mg/kg with fenthion, its sulfoxide and sulfone, oxon sulfoxide and oxon sulfone and stored below -20°C for over a year.

Samples were extracted with acetone or acetone/water and residues determined by the methods of Ohs (1990, 1991b). At intervals the stored samples and freshly prepared spiked samples were analysed and the results compared (Table 13).

Table 13. Stability of fenthion residues in frozen orange peel and pulp.

Orange peel			Orange pulp		
Day	Residues, found/added, %		Day	Residues, found/added, %	
	Stored	Fresh		Stored	Fresh
0	94.6	93.5	0	61.5	66.4
128	77.3	91.7	7	96.8	105
260	80.2	85.0	143	79.9	88.6
433	109	94.3	275	71.9	81.6
			448	117	87.2

The residues of fenthion and the four metabolites were stable in orange peel and pulp for at least 14 months when stored below -20°C.

Animal products. The stability of fenthion and its oxon sulfone in the presence of animal tissues was evalutated by Olson (1966). Cattle brain, fat, heart, kidneys, liver and muscle (steak) were separately spiked with [^{32}P]fenthion and [^{32}P]fenthion oxon sulfone at about 1-2 mg/kg and the spiked samples stored at -18°C for 0, 2, and 4 weeks (fenthion) and 0, 2, 4, and 6 weeks (oxon sulfone). The samples were extracted with chloroform and the chloroform and water phases radioassayed. The recoveries of the radiolabel from tissues freshly spiked with [^{32}P]fenthion at 1.86 mg/kg were brain 86.2%; fat 76.7%; heart 94.7%; kidney 91.2%; liver 82.6%; muscle 91.0%. The corresponding recoveries of from tissues freshly spiked with the oxon sulfone at 1.27 mg/kg were brain 88.2%; fat 91.2%; heart 93.3%; kidney 88.9% liver 87.4%; muscle 89.8%.

In the samples stored at -18°C, the ^{32}P found in the chloroform and water phases was expressed as a percentage of the total ^{32}P recovered from the freshly spiked samples. Fenthion was stable in all tissues for at least a month. More than 83% of the radioactivity remained in the chloroform phase over the trial period in all samples except muscle where 68.8% of the radioactivity was in the chloroform phase and 0.9% in the water phase after 2 weeks, although the respective values were 105.1% and 1.1% after 4 weeks. Less than 2.5% of the radioactivity was found in the water phase from any sample except fat at 4 weeks. At that time the distribution reported in the fat was 116.2% chloroform-soluble, 12.3% water-soluble, total activity 128.5% of the original.

Radioactive assay indicated that fenthion oxon sulfone was stable for 6 weeks in brain, heart, muscle and fat stored at -18°C, with more than 77% of the radiolabel in the chloroform phase. Between 4 and 9% of the radiolabel was in the water phase from all samples except fat at 6 weeks from which 86% was in the chloroform phase and 14.4% in the water phase, a total activity of 100.4%. In the kidneys and liver the reported distributions were as shown below.

Storage	Kidneys		Liver	
time	$CHCl_3$	water	$CHCl_3$	water
0	95.7%	4.3%	71.8%	28.2%
2 weeks	79.5%	5.2%	47.8%	33.4%
4 weeks	68.6%	5.4%	29.5%	40.3%
6 weeks	68.4%	6.8%	22.3%	48.2%.

These results indicate marginal storage stability in the kidneys and instability in the liver.

The short-term stability of residues of fenthion and its oxon sulfone in cattle tissues at room temperature has been investigated (Olson, 1973). Fresh muscle, liver and fat were fortified at 1 mg/kg with fenthion or fenthion oxon sulfone and allowed to stand in darkness at room temperature for 6 hours. Samples were taken during that period and residues extracted and determined according to the method of Thornton (1967). Fenthion was stable in all the tissues: after 6 hours 96% of the original concentration remained in the liver and muscle and 83% in the fat. Fenthion oxon sulfone was stable in muscle and fat (88% and 107% after 6 hours), but was rapidly lost from liver with 25% decomposition after one hour and about 85% loss after 4 hours.

In a goat metabolism study (Weber and Ecker, 1992), it was noted that fenthion and its metabolites in samples stored at about -20°C for an unspecified time underwent further degradation to form more oxidized, demethylated and dephosphorylated product. Details of the study are provided in the "Metabolism and environmental fate" section.

The stability of fenthion and fenthion sulfone residues in frozen tissues from sheep treated with fenthion by topical application was investigated by Cameron *et al.* (1995). Sheep given single applications at 20 mg fenthion/kg bw were killed at various times to allow the determination of fenthion and fenthion sulfone in the tissues. The percentages of fenthion remaining after storage at approximately -20°C for 51 weeks were quite low, for example 16-38% in liver, kidneys, muscle and subcutaneous fat at 0.04 mg/kg and 9-50% at 0.2 mg/kg. Fenthion was less stable in muscle than in the other tissues. These results suggested substantial instability during frozen storage.

The percentages of fenthion sulfone remaining in tissues fortified at the same levels as fenthion and stored at approximately -20°C for 52 weeks were 76-109% at 0.04 mg/kg and 59-76% at 0.2 mg/kg. Fenthion sulfone is considered to be stable for at least 52 weeks when stored under freezer conditions.

In tissues freshly spiked with 0.02, 0.04, 0.1 and 0.2 mg/kg, recoveries of fenthion and fenthion sulfone at all levels were good, with mean recoveries of 77.4-84% of the added fenthion and 82.1-90.4% of fenthion sulfone.

Because the residues in the tissues fortified with fenthion and stored frozen suggested a lack of stability, the tissues from the residue study which had also been stored would have been expected to show a similar loss. A number of stored samples of each tissue from the fenthion residue study were reanalysed. The maximum time between the original sampling and analysis was 40 weeks and the minimum time between the original analysis and reanalysis was 46 weeks.

The ratios of the fenthion residues found on reanalysis to those found originally were variable (about 62-156%), indicating that excessive loss of fenthion had not occurred.

Residue definition

The studies on animal and plant metabolism and environmental fate indicated that the use of fenthion would be expected to result in the presence of fenthion and fenthion oxon and their sulfoxides and sulfones under various conditions. Methods are available to measure these residues readily and accurately to the desired limits of determination, either individually or as fenthion oxon sulfone, which allows relatively easy determination of compliance with MRLs.

The inclusion of the principal oxidative metabolites of fenthion in the residue definition is clearly important because they are more active cholinesterase inhibitors than is fenthion.

No change is recommended to the current Codex definition of the fenthion residue.

USE PATTERN

Fenthion's insecticidal properties derive from contact, stomach and respiratory action as a cholinesterase inhibitor. Fenthion has been used since 1957 for the control of a wide range of insect pests including fruit flies, leafhoppers, leaf miners, leaf-eating larvae and cereal bugs in fruit, vines, olives, vegetables, cotton, tea, sugar cane, beet, and rice. The use pattern also includes the post-harvest disinfestation of fruit, the control of insect pests (e.g. mosquitoes, fleas) in public health situations and animal houses and for the control of animal ectoparasites.

Information on use patterns in crops (Table 14) was provided by the sponsor and the governments of Australia, Canada, New Zealand, Peru and The Netherlands. Table 15 lists the use patterns on animals and in animal houses provided by the sponsor, Australia, Canada and New Zealand.

Table 14. Registered uses of fenthion on crops.

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Alfalfa	Greece	EC	spray	0.5-0.6		1	14
Alfalfa	Peru				0.3		14
Adzuki beans	Japan	EC	spray		0.034 - 0.05	1-4	21
Adzuki beans	Japan	DP	spray	0.6-0.8		1-4	21
Almonds	Greece	EC	spray	1.25	0.06	1	14
Apple	Australia	EC	spray		0.05	m[1]	7
Apple	Australia	EC	spray		0.083	3	7
Apple	Belgium	EC	spray	1.24	0.082	1	21
Apple	France	EC	spray	0.55	0.055	1	15
Apple	France	EC	spray	0.825	0.0825	1-2	15
Beets (*Beta vulgaris)*	Belgium	EC	spray	0.825-2.48		1	21
Beets (*Beta vulgaris)*	France	EC	spray	0.55		1	15
Beets (*Beta vulgaris)*	Spain	EC	spray		0.05 -0.1	1	30
Beets (*Beta vulgaris)*	Spain	WP	spray		0.06-1	1	30
Beet, sugar	Austria	EC	spray	0.375		1-2	35
Beet, sugar	Greece	EC	spray	0.75	0.15	1	14
Capsicums	Australia	EC	spray	0.41	0.041	m	7
Capsicums	Australia	EC	flood spray or dip		0.041		na[2]
Cereals	Greece	EC	spray	0.5-1		1	14
Cereals, stored	Peru	SP		0.2-0.3			
Celery	Belgium	EC	spray	0.5	0.082	1	21
Celery	Peru	EC			0.2		14
Cherries (sweet & sour)	Belgium	EC		1.24	0.082	1	21
Cherries (sweet & sour)	France	EC		0.55		1	15
Cherries (sweet & sour)	Germany	EC		0.79	0.052	1	14
Cherries (sweet & sour)	Italy	EC		0.25-0.5	0.025-0.05	1-2	28
Cherries (sweet & sour)	Northern European[3]	EC		0.79	0.05	1	14
Chicory, Witloof	Belgium	EC	spray	0.5	0.082	1	21
Citrus fruits	Algeria	EC	+ bait	0.16		1-2	21
Citrus fruits	Australia	EC	spray		0.04	2	7
Citrus fruits	Australia				0.083	3	7
Citrus fruits	Brazil	EC	+ bait	0.075		1	21
Citrus fruits	Brazil	EC		0.4	0.05	2-6	21
Citrus fruits	Brazil	EW	+ bait	0.075		1	21
Citrus fruits	Brazil	WP	+ bait	0.05		3-8	21
Citrus fruits	Brazil	WP		0.25	0.05	3-8	21
Citrus fruits	Costa Rica	EC		0.5-1.25	0.05-0.12	1-3	15
Citrus fruits	Cuba	EC		0.75	0.075	1-2	15
Citrus fruits	El Salvador	EC		0.5-1	0.05-0.1	1-2	15
Citrus fruits	Greece	EC	ground + bait	0.18	0.3	3-5	14
Citrus fruits	Greece	EC		1.5	0.05	1-2	14
Citrus fruits	Guatemala	EC		0.5-1.25	0.05-0.12	1-3	15
Citrus fruits	Honduras	EC		0.5-1.25	0.05-0.12	1-3	15
Citrus fruits	Italy	EC		0.25-0.5	0.025-0.05	1-2	28
Citrus fruits	Jordan	EC	+ bait	0.015-0.03		1	21
Citrus fruits	Jordan	EC	full cover	1-1.5	0.05-0.075	1	21
Citrus fruits	Kuwait	EC	+ bait	0.015-0.03		1	14
Citrus fruits	Kuwait	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Libya	EC	+ bait	0.015-0.03		1	14
Citrus fruits	Libya	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Mexico	EC		0.6	0.06	1-2	21

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
	(oranges only)						
Citrus fruits	Southern European[3]	EC	full cover	0.5	0.05	2	28
Citrus fruits	Southern European[3]	EC	aerial + bait	0.06	0.86	2	3
Citrus fruits	Oman	EC	+ bait	0.015-0.03		1	14
Citrus fruits	Oman	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Peru	EC	+ bait		0.2-0.3	1-3	21
Citrus fruits	Peru	EC	full cover		0.4	1-3	14
Citrus fruits	Portugal (oranges only)	EC		0.55-0.72	0.055-0.072	1-4	14
Citrus fruits	Saudi Arabia	EC	+ bait	0.15-0.3		1	14
Citrus fruits	Saudi Arabia	EC		1-2	0.05-0.1	1	14
Citrus fruits	Spain	EC	aerial + bait	0.06	0.86	1-2	3
Citrus fruits	Spain	EC	ground + bait	0.3	0.3	1-2	30
Citrus fruits	Spain	WP	spray	0.9-1.5	0.06-0.1	1-2	30
Citrus fruits	Spain	WP	+ bait	-	0.3	1-2	30
Citrus fruits	Sri Lanka	EC		0.5-1		1-2	
Citrus fruits	Taiwan	EC	+ bait on single trees	0.02		2-3	na
Citrus fruits	Tunisia	EC	+ bait	3.4		1-2	14
Citrus fruits	UAR	EC	+ bait	0.015-0.03		1	14
Citrus fruits	UAR	EC	full cover	1-1.5	0.05-0.075	1	14
Citrus fruits	Uruguay	EC		1.05	0.058	1-2	20
Coffee bush	Peru	EC			0.2		14
Common bean[4]	Belgium	EC	spray	0.5	0.082	1	21
Common bean[4]	Peru	EC			0.2		14
Cucurbits	Australia	EC	dip		0.041	1	na[2]
Deciduous fruit	Australia	EC	spray		0.04	2 & 5	7
Deciduous fruit	Australia	EC	spray		0.052	m	7
Egg plant	Australia	EC	spray	0.4	0.04	m	7
Figs	Australia	EC	spray		0.04	2	7
Forage crops & grasses, rangeland (see also Pastures)	Canada	EC		0.055-0.11		as needed, 3 weeks between applns.	3 day withholding period
Fruit	Austria	EC	spray	1.12	0.075	1-2	35
Fruit	Belgium	EC	spray	1.24	0.082	1	21
Fruiting vegetables other than cucurbits	Australia	EC	dip		0.041	1	na[2]
Fruit trees	Australia	EC	spray		0.041		7
Garlic	Peru	EC			0.2		14
Grapes	Australia	EC	spray		0.04	2 & m	7
Grapes	Austria	EC	spray	0.75	.075	1-2	35
Grapes	Spain	EC	spray	0.35-0.7	0.05-0.1	1-2	30
Grapes	Spain	EC	spray	1	0.1	1	14-21
Grapes	Spain	WP	spray	0.3	0.3	1-2	14-21
Grapes	Spain	WP	spray		0.3	1-2	30
Guava	Australia	EC	spray		0.041	m	14
Hops	Belgium	EC	spray	4.12	0.082	1	21
Kiwifruit	Australia	EC	spray		0.041	m	7
Leeks	Belgium	EC	spray GIS	0.5	0.082	1 & 2-3	21
Loquats	Australia	EC	spray		0.04	m	7
Lychees	Australia	EC	spray		0.05	m	7

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Olives	Algeria	EC	+ bait	0.21-0.32		1	21
Olives	Croatia	EC		0.5-0.75	0.05-0.75	3	28
Olives	France	EC	spray	0.55	0.055	1-2	21
Olives	Greece	EC	ground + bait	0.07	0.3	3-5	21
Olives	Greece	EC	aerial + bait	0.09	0.9	3-5	21
Olives	Greece	EC		0.75	0.05	2	30
Olives	Italy	EC	spray	0.25-0.5	0.025-0.05	2-3	28
Olives	Jordan	EC		0.75-1.5	0.05-0.1	1	30
Olives	Kuwait	EC	+ bait	0.015-0.03		1	21
Olives	Kuwait	EC		0.75-1.5	0.05-0.1	1	21
Olives	Libya	EC	+ bait	0.005-0.03		1	21
Olives	Oman	EC	+ bait	0.015-0.03		1	21
Olives	Oman	EC		0.75-1.5	0.05-0.1	1	21
Olives	Portugal	EC	for cannery	0.55	0.055	1	21
Olives	Portugal	EC	direct consumption	0.55	0.055	1-2	42
Olives	Saudi Arabia	EC	+ bait	0.15-0.3		1	21
Olives	Slovenia	EC		0.5-0.75	0.05-0.075	1-3	28
Olives	Southern European[3]	EC	ground + bait	0.07	0.3	3-5	21
Olives	Southern European[3]	EC	aerial + bait	0.09	0.9	3-5	21
Olives	Southern European[3]	EC	full cover	0.25-0.5	0.025-0.05	3	28
Olives	Southern European[3]	EC	early appln.	1.25	0.08	1-2	90
Olives	Tunesia	EC	+ bait	0.56 - 0.83		1	21
Olives	Turkey	EC		0.52- 0.79	0.05-0.078	1-3	21
Olives	UAR	EC	+ bait	0.015-0.03		1	21
Olives	UAR	EC		0.75-1.5	0.075-0.15	1	21
Olives	Yugoslavia	EC		0.5-0.75	0.05-0.075	1-3	21
Onions, Bulb	Belgium	EC	spray	0.5	0.082	1 and 2-3	21
Onions, Bulb	Peru	EC			0.2		14
Orange	Portugal	EC	spray	0.55-0.72	0.055-0.072	1-4	14
Orange	Mexico	EC		0.6		1-2	21
Papaws	Australia	EC	spray		0.041	m	14
Pastures	Australia	EC	spray	0.28		m	7
Pastures (See also Forage crops)	Australia	EC	spray	0.55		m	7
Pea, garden	Belgium	EC	spray	0.74	0.082	1	21
Peach	Belgium	EC	spray	1.24	0.082	1	21
Peach	Brazil	EC		0.5	0.05	3-8	21
Peach	France	EC	spray	0.55	0.055	1-2	15
Peach	France	EC	spray	0.82	0.082	1-2	15
Peach	Greece	EC	spray	1.25	0.05	1	14
Peach	Israel	EC		0.5 -1.5	0.05-0.15	1	21
Peach	Italy	EC	spray	0.25 -0.5	0.025 -0.05	1-2	28
Peach	Peru	EC		0.5-1	0.05-0.4	1-4	14
Peach	Portugal	EC	spray	0.55	0.055	1-3	14
Peach	South Africa	EC		1.4 -1.75	0.04-0.05	1-3	10
Peach	Southern European[3]	EC		0.5-1.125	0.03-0.075	2	28
Peach	Spain	EC	spray	1 -1.12	0.1-0.112	1-2	14

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Peach	Turkey	EC		2.4	0.08	1-2	21
Peach	Zimbabwe	EC		0.6-0.9	0.03-0.045	1-3	10
Pear	Australia	EC	spray		0.052	m	7
Pear	Australia	EC	spray		0.083	2 & 3	7
Pear	Belgium	EC	spray	1.24	0.082	1	21
Pepinos	Australia	EC	spray		0.041	m	7
Persimmon	Australia	EC	spray		0.04 & 0.05	5 & m	7
Pistachio	Greece	EC	spray	0.75	0.05	1-2	14
Plums (including prunes)	Belgium	EC	spray	1.24	0.082	1	21
Pome fruit	Spain	EC	spray	0.75-1.5	0.05-0.1	1-2	30
Pome fruit	Spain	EC	spray	0.75-1.5	0.05-0.1	1-2	30
Pome fruit	Spain	EC	spray + bait		0.05-0.3	1-2	30
Pome fruit	Spain	WP	spray	0.9-1.5	0.06-0.1	1	30
Pome fruit	Spain	WP	+ bait		0.06-0.1	1	30
Potato	Belgium	EC	spray	0.33	0.082	1	21
Potato	Japan	EC	spray		0.05	1-2	7
Prunus laurocer	Belgium	EC	spray	1.24	0.082	1	21
Quince	Australia	EC	spray		0.083	2 & 3	7
Rape	Austria	EC	spray	0.3		1	35
Rape	Belgium	EC	spray	0.5	0.082	1	21
Rice	Colombia	EC		0.38-0.75		1-3	14
Rice	Costa Rica	EC		0.5-1		2-3	15
Rice	El Salvador	EC		0.3-0.6		1	15
Rice	Guatemala	EC		0.5-1.4		1-2	15
Rice	Japan	EC		0.375-0.75	0.034-0.05	1-2	30
Rice	Japan	WP		0.4-0.75	0.04-0.05	1-2	30
Rice	Japan	GR		1.5-2		1-2	45
Rice	Japan	DP		0.6-0.8		1-2	21
Rice	Kuwait	EC		0.4-0.75		1	14
Rice	Libya	EC		0.4-0.75		1	14
Rice	Malaysia	EC		0.3-0.4		1-3	14
Rice	Mexico	EC		0.6-1		1-2	30
Rice	Panama	EC		0.7-1		1-2	15
Rice	Oman	EC		0.4-0.75		1	14
Rice	Peru	EC	Spray	0.4-0.75	0.2-0.4	1-2	15
Soya bean	Japan	EC	spray		0.034- 0.05	1-3	45
Soya bean	Japan	DP	spray	0.6-0.8		1-3	45
Stone fruit	Australia	EC	spray		0.041	2 & 3	7
Stone fruit	Australia	EC	spray		0.041-0.052	m	7
Stone fruit	Greece	EC	spray	1.25	0.05	1	14
Stone fruit	Spain	EC	spray	0.75-1.5	0.05 -0.1	1-2	30
Stone fruit	Spain	EC	spray	1-1.125	0.05-0.1	1-2	30
Stone fruit	Spain	EC	spray + bait		0.05-0.3	1-2	30
Stone fruit	Spain	WP		1-1.125	0.1	1-2	30
Stone fruit	Spain	WP		0.9-1.5	0.06-0.1	1-2	30
Stone fruit	Spain	WP	+ bait	1-1.12	0.3	1-2	30
Sub-tropical/tropical fruit, inedible peel	Australia	EC	spray		0.041	5	7
Sub-tropical/tropical fruit, inedible peel	Australia	EC	dip		0.041	1	na (5)
Sugar cane	Japan	EC	drench soln.		0.05 -0.1	1-2	200
Sugar cane	Japan	GR	add to soil	4.5		1-2	200
Sweet potato	Japan	GR	add to soil	4.5		1-2	30

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray concn., kg ai/hl	No.	
Sweet potato	Japan	DP	spray	0.6-0.8		1-2	45
Tomato	Australia	EC	spray	0.41	0.041	m	7
Tomato	Peru	EC			0.2		14
Useful plants	Belgium	EC	spray		0.082	1	21
Vegetables	Belgium	EC	spray	0.74	0.082	1	21
Yam	Japan	GR	Add to soil	4.5		1-3	45 days

[1] Multiple: repeat as necessary
[2] Not applicable, quarantine treatment only
[3] Use pattern as proposed by sponsor
[4] Pods and/or immature seeds

Information on GAP for uses on ornamental plum, roses, tobacco, and weeping willow was provided but is not included in the Table.

The sponsor advised that the use of fenthion on the following crops would no longer be supported in EU Member States: alfalfa, almonds, beans, beet (fodder and sugar crops), celery, cereals, chicory, grapes, hops, leeks, onions, peas, pistachio, pome fruit, potatoes, rape, stone fruit except cherries and peaches, tobacco and vegetables. Uses on cherries, citrus fruits, olives and peaches (and ornamentals) were the only ones which would to be retained. The use patterns to be proposed are included in Table 14.

Table 15. Registered uses of fenthion on animals, animal houses and other buildings.

Animal or building treated (pest controlled)	Country	Form[1]	Rate, mg ai/kg bw	No. of treatments	Withholding period, days
Cattle (grub)	Algeria	PO	5-10	1[2]	14 (edible tissues) 5 (milk)
Cattle,non-lactating (lice)	Argentina	SO	8	1 (additional if needed)	28 (edible tissues)
Cattle (lice)	Australia	PO, SA	~ 4-10	1 (additional if needed)	10 (meat) No milk WHP
Cattle (cattle grub, lice)	Belgium	PO, SA	10 (PO) 5 (SA)	1[2]	14 (edible tissue) 5 (milk)
Cattle, non-lactating (Dermatobia, Myiasis, lice)	Brazil	SO	10.5-15	1 (additional if needed)	14 (edible tissues)
Cattle, beef & non-lactating (lice, cattle grub)	Canada	SN	5-8	1-2	45 days (spot-on) For the PO 35 days for a single treatment, 45 days if two treatments for lice are used.
Cattle (lice)	Chile	SO	8	1 (additional if needed)	14 (edible tissues) 5 (milk)
Cattle (Dermatobia, lice, biting flies)	Colombia	SO	5-16	1 (additional if needed)	Not stated
Cattle, non-lactating (Dermatobia, lice, biting flies)	Costa Rica	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle, non-lactating (Dermatobia, lice, biting flies)	Dominican Republic	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle (cattle grub, lice)	Eire	SA	8	1[2]	21 (edible tissue) 5 (milk)
Cattle (cattle grub, lice)	France	PO, SA	5	1[2]	14 (edible tissue) 5 (milk)
Cattle, non-lactating (Dermatobia, lice, biting flies)	Guatemala	SO	5-16	1 (additional if needed)	15 (edible tissues)

Animal or building treated (pest controlled)	Country	Form[1]	Rate, mg ai/kg bw	No. of treatments	Withholding period, days
Cattle, non-lactating (Dermatobia, lice, biting flies)	Honduras	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle, non-lactating (Dermatobia, lice, grub)	Mexico	SO	5-16	1 (additional if needed)[2]	14 (edible tissues)
Cattle, non-lactating (lice)	New Zealand	PO	Up to 4.5	as needed	21
Cattle, non-lactating (Dermatobia, lice, biting flies)	Nicaragua	SO	5-16	1 (additional if needed)	15 (edible tissues)
Cattle (lice, Myiasis)	South Africa	SO	5	1 (additional if needed)	14 (edible tissues) 7 (milk)
Cattle (grub)	Turkey	SO, PO	5-10	1[2]	14 (edible tissues) 5 (milk)
Cattle (cattle grub, lice)	UK	PO	10	1[2]	21 (edible tissues) 5 (milk)
Cattle, non-lactating	Uruguay	SO	8	1 (additional if needed)	28 (edible tissues)
Cattle, beef (grub, lice, biting flies)	USA	SO, PO	5.5-11	1 (additional if needed 35 days later)	45 (edible tissues)
Cattle (Dermatobia, lice, biting flies)	Venezuela	SO	5-16	1 (additional if needed)	not stated
Pigs (lice)	Belgium	SA	5	1[2]	8 (edible tissue)
Swine (hogs, pigs) (lice)	Canada	SN	9.75	1	14
Sheep (lice, Myiasis)	South Africa	SO	5	1 (additional if needed)	14 (edible tissues) 7 (milk)
Farm buildings, piggeries, poultry houses (insects)	Canada	EC	1.5 kg ai/hl	As necessary	1.5
Rooms & storage sheds	Peru	SP	200-400 kg ai/ha		

[1] PO = pour-on; SA = spot-on; SN = solution; SO = spreading oil; SP = water soluble powder
[2] A repeat treatment may be necessary 10-14 days later to eradicate lice which have hatched from eggs present at first treatment

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting was supplied with residue data from supervised trials on various fruits and vegetables, cattle, sheep, and pigs. Data on residues in milk were also provided. Underlined residues in the Tables are from treatments considered to be according to GAP.

Plant commodities

Data were supplied on pre-harvest applications to cherries, mandarins, olives, oranges, peaches and rice, and on post-harvest trials on capsicums, cucumbers, mangoes, rockmelons, tomatoes and zucchini.

Citrus fruits. Results from 8 residue trials conducted in Spain on mandarins as single ultra-low-volume or low-volume aerial applications with bait were presented. The results are shown in Table 16. Plot sizes, when reported, ranged between 1000 and 10000 sq m. Fruit were sampled at or near maturity.

Residues were not detectable in the pulp (<0.02 mg/kg in 1981, <0.01 mg/kg in 1992). Residues in the whole fruit were calculated from those in the pulp and peel. Blank values on the peel at 3 days PHI were all <0.01 mg/kg.

The 1992 trials were considered to be within Spanish GAP for the aerial application of fenthion with bait to citrus fruits (0.06 kg ai/ha with a 3-day PHI and 1 or 2 applications).

Table 16. Total residues of fenthion in mandarins from supervised trials in Spain using a single low-volume aerial application of a 500 EC formulation.

Year, variety	Application		PHI, days	Residues, mg/kg, means		Report No., method, LOD
	kg ai/ha	kg ai/hl		Whole fruit	Peel	
1969 Satsuma	0.15 aerial + bait	0.75	0 7 14	<0.1 <0.1 <0.1	0.25 <0.1 <0.1	0329-69 Determined as P 0.1 mg/kg
1969 Clementine	0.15 aerial + bait	0.75	0 7 14 28	0.25 0.22 0.13 0.08	0.73 0.60 0.29 0.20	0360-69 GLC 0.05 mg/kg
1969 Satsuma	0.15 aerial + bait	0.75	0 7 14 28	0.39 0.20 0.12 0.04	1.25 0.34 0.19 0.14	0361-69 GLC 0.05 mg/kg
1981 Satsuma	0.19 aerial + bait	0.94	0 14 21 28 35	0.39 0.41 0.26 0.13 0.10	1.31 1.42 0.9 0.48 0.31	5000-81 Olson 1982 0.02 mg/kg
1981 Satsuma	0.094 aerial + bait	0.47	0 14 21 28 35	0.35 0.27 0.13 0.15 0.1	1.16 0.96 0.48 0.48 0.31	5001-81 As for 5000-81
1992[1] Clausellina	0.052 aerial + bait	0.74	0 3 13	0.02 <u>0.02</u> <u>0.02</u>	0.07 0.08 0.11	RA-2101/92 205842 Bayer No. 0584/92 Olson 1991 & Ohs 1991 0.01 mg/kg
1992[1] Clausellina	0.052 aerial + bait	0.74	0 3 13	0.09 <u>0.04</u> <u>0.21</u>	0.38 0.20 1	205850 Bayer No.0585-92 As for RA-2101/92
1992[1] Clausellina	0.052 aerial +bait	0.74	0 3 13	0.03 <u>0.04</u> <u><0.01</u>	0.10 0.18 0.02	205869 Bayer No. 0586-92 As for RA-2101/92

[1] Ohs and Walz-Tylla, 1993. Day 3 was the regular day of harvest

Results from 7 residue trials on <u>oranges</u> in Spain as single low-volume or ultra-low-volume aerial applications with bait were presented (Table 17). Fruit were harvested either at or several weeks before maturity. In the pre-1992 trials the area treated was not recorded or was small (100 sq. m.). In the 1992 trials the treated areas were 4000 sq m.

Table 17. Total residues of fenthion in oranges from supervised trials in Spain following a single treatment with an EC formulation.

Year, variety	Application		PHI, days	Residues, mg/kg, means		Report No., Method, LOD
	kg ai/ha	kg ai/hl		Whole fruit	Peel	
1969 Navel Tompson	0.15 aerial + bait	0.75	0 7 14	<0.1 <0.1 <0.1	0.20 0.15 0.20	0328-69 Determined as P, 0.1 mg/kg
1969 Navel	0.15 aerial + bait	0.75	0 7	0.04 0.06	0.12 0.13	0357-69 GLC 0.05 mg/kg

Year, variety	Application		PHI, days	Residues, mg/kg, means		Report No., Method, LOD
	kg ai/ha	kg ai/hl		Whole fruit	Peel	
			14 28	0.02 0.02	0.07 0.05	
1990 Navelina	0.052 aerial + bait	0.74	0 14	<0.01 <u><0.01</u>	<0.01 <0.01	0496-90 Olson 19981 & Ohs, 1988 0.01 mg/kg
1990 Navelina	0.052 aerial	0.74	0 14	0.03 <u><0.01</u>	0.13 0.02	0736-90 As for 0496-90
1992[1] Valencia Late	0.052 aerial + bait	0.74	0 3 14	0.75 <u>0.18</u> <u>0.10</u>	2.8 0.69 0.34	RA-2101 /92 205818 Bayer No. 0581-92 As for 496-90
1992[1] Valencia Late	0.052 aerial + bait	0.74	0 3 14	0.98 <u>0.15</u> <u>0.11</u>	3.4 0.56 0.42	205826 Bayer No. 0582-92. As for 496-90
1992[1] Valencia Late	0.052 aerial + bait	0.74	0 3 14	0.09 <u>0.05</u> <u>0.04</u>	0.27 0.14 0.12	205834 Bayer No. 0583-92. As for 496-90.

[1] Ohs and Walz-Tylla, 1993. Day 3 was the regular day of harvest

In the 1990 and 1992 trials the residues in the pulp were all <0.01 mg/kg. In the 1992 trials, residues in the whole fruit were calculated from those in the pulp and peel. Blank values in the 1990 trials were <0.01 mg/kg. In the 1992 trials, the orange peel control values were high (0.80, 0.05, and 0.38 mg/kg at 3 days PHI; 0.19, 0.42, and 0.32 mg/kg at 14 days). These high values were ascribed to the control plots between treated bands being contaminated by aerial drift. Residues in the pulp of control samples were all <0.01 mg/kg. Calculated whole fruit residues in the controls at a 3-day PHI were 0.22, 0.02, and 0.14 mg/kg. Although reported, these control values were not subtracted from the values measured in the treated samples. The 1990 and 1992 trials were again considered to be within Spanish GAP for the aerial application of fenthion to citrus fruit.

<u>Cherries</u>. Ten supervised trials were carried out in Germany. The results are shown in Table 18.

Table 18. Total residues of fenthion in cherries from supervised trials in Germany using single applications of a 500 EC formulation (1968-9) and a 550 EC formulation (1978-9).

Year, variety	Application		PHI, days	Residues, mg/kg, means	Reference, Method, LOD
	kg ai/ha	kg ai/hl			
1968 Sweet cherry	1[1] (1.25 g/tree)	0.05	0 7 10 14	5.05 0.95 0.55 <u>1.0</u>	89-68 Determined as P, 0.05 mg/kg
1968 Sweet cherry	1[1] (1.25 g/tree)	0.05	0 7 9 14	4.75 0.95 0.3 <u>0.55</u>	90-68 As for 89-68
1968 Sour cherry	1[1] (1.25 g/tree)	0.05	0 7 10 14	4.6 0.65 0.5 <u>0.5</u>	91-68 As for 89-68
1968 Sour cherry	1[1] (1.25 g/tree)	0.05	0 7 10 14	5.4 1.25 0.9 <u>0.6</u>	92-68 As for 89-68

Year, variety	Application		PHI, days	Residues, mg/kg, means	Reference, Method, LOD
	kg ai/ha	kg ai/hl			
1969 Schwarze Knorpel	15 g/tree	30 l/tree (0.05 kg ai/hl)	1 8 14	4.8 0.6 <u>0.8</u>	235-69 As for 89-68
1969 Schwarze Knorpel	7.5 g/tree	30 l/tree (0.025 kg ai/hl)	1 8 14	2.4 0.8 0.35	236-69 As for 89-68
1978 Schatten Morelle	1.1	0.05	0 4 7 14 21	4.2 1.8 0.99 <u>0.32</u> <u>0.38</u>	5000-78 Olson[2] 0.01 mg/kg
1978 Schatten-morelle	1	0.05	0 4 7 14 21	4.0 1.4 0.66 <u>0.65</u> <u>0.35</u>	5001-78 As for 5000-78
1978 Heimanns Rubin-weichsel	1	0.1	0 4 7 14 21	5.6 4.1 1.0 1.1 0.47	5002-78 As for 5000-78
1979 Schatten-morelle	0.82	0.06	0 5 8 15 21	0.03 0.02 <0.01 <0.01 <0.01	5000-79 Only fenthion oxon sulfone determined

[1] Application rates were 1.25 g ai/tree, calculated by sponsor to be approximately 1 kg ai/ha. 2.5 litres were applied per tree so that the concentration was 0.05 kg ai/hl
[2] Method described as: T.J. Olson modified laboratory method (I 127): Chemagro Report Nr 20 417, 1968

The number of trees treated in the trials was between 4 and 8 except in trial number 5000-79 where 0.5 ha was treated.

Single applications were used in all trials. Spray dilutions were 0.05 kg fenthion/hl (7 trials), 0.06 kg/hl (one trial), 0.1 kg/hl (one) and 0.025 kg/hl (one).

Trials at 0.05 kg ai/hl complied with the registered German use pattern of a single application at 0.05 kg fenthion/hl with a 14-day PHI. The 1979 trial (5000-79, conducted at 0.06 kg ai/hl) was excluded as only fenthion oxon sulfone was determined.

In the trials according to German GAP, the initial residues were about 5 mg/kg which decreased to about 0.3-1 mg/kg after 14 days. Residues at 21 days were 0.35 and 0.38 mg/kg. In the 1979 trial (5000-79) in which a normal application rate was used but only the oxon sulfone was determined, residues were low from day 0 and not detectable by day 8. This showed that this metabolite made a negligible contribution to the residue.

<u>Peaches</u>. Supervised trials were carried out in Spain (four trials) and South Africa (one trial). All were according to GAP (0.04-0.05 kg ai/hl, 1-3 sprays, 10-day PHI in South Africa, 0.1-0.112 kg ai/hl, 1-2 sprays, 14-day PHI in Spain, although there were no results at 10 days from South Africa and only one at 14 days from Spain. The results are shown in Table 19.

In the Spanish trials the areas treated were between 75 and 120 sq m. Spraying was by a power-operated knapsack sprayer. In the 1993 trials control values were all less than 0.01 mg/kg except one of 0.02 mg/kg which was attributed to spray drift on to the control trees. Residues were all calculated from replicate analyses of the pulp and peel. A fenthion half-life of 1.6 days was calculated in 1993.

Table 19. Total residues of fenthion in peaches from supervised trials in Spain and South Africa with one or two applications of a 500 EC formulation.

Country, year, variety	Application			PHI, days	Residues, mg/kg	Report, Method, LOD
	No.	kg ai/ha	kg ai/hl			
South Africa 1986 Variety not stated	1	1.88	0.06	0 7 14 21 29 35	4.8 2.2 1.1 0.44 0.23 0.11	311/ 88946/ C194 Frehse *et al.*, 1962b 0.05 mg/kg
Spain 1990 Agosto	2	1	0.1	0 20	1.7 b0.40 0.48 b0.35	0342-90 Ohs[1] 0.01 mg/kg
1993 July Lady	2[2]	1.125	0.075	0 0 10 14 21 28	0.30[3] 0.99 b<0.01 0.20 0.16 0.08 0.05 b<0.01	304301 (Bayer 0430-93) Ohs, 1994b 0.01 mg/kg
1993 Caterine	2[2]	1.05, 1.125	0.075	0 28	2.3 b<0.01 0.12 b<0.01	304328 (Bayer 0432-93) As for 304301
1993 Laura	2[2]	1.125	0.075	0 24	1.9 b<0.01 0.24 b<0.01	304336 (Bayer 0433-93) As for 304301

[1] Method described as Ohs, P. MR 20417, 27 April 1967 (revised: 11 September 1984) which the sponsor advised was the reference Ohs, 1990
[2] 21 days between applications
[3] Before last treatment
b = blank

Olives. The results of supervised trials in Greece, Italy and Spain are shown in Table 20.

In Spain the areas treated were 20 ha in trial 314-69 and 70 ha in trial 196-70, in Greece 600 hectares were sprayed in the 1984 trial and 2000 sq m in the 1988 trials, and in Italy 4000 sq m in trial 279-90, 640 sq m in trial 712-90, and 10 plants in trial 713-90.

Table 20. Total residues of fenthion in olives from supervised trials in Spain, Greece and Italy.

Country, year, form., variety	Application			PHI, days	Residues, mg/kg, means, in fruit	Report no., Method of analysis, LOD
	No.	kg ai/ha	kg ai/hl			
Spain 1968 50 EC Zorzaleno	2	0.3 ULV, ground, full cover + bait	1.5	4 10	0.25 0.1	381A-68 Determined as P 0.1 mg/kg
Spain 1968 50 EC Zorzaleno	3	0.3 ULV, ground, full cover + bait	1.5	14 28	<0.1 <0.1	381A-68-1 As for 381A-68
Spain 1969 50 EC Farga	2	0.15 ULV, aerial + bait	0.75	1 8 15	<0.05 <0.05 <0.05	314/69 Determined as P 0.05 mg/kg

Country, year, form., variety	Application			PHI, days	Residues, mg/kg, means, in fruit	Report no., Method of analysis, LOD
	No.	kg ai/ha	kg ai/hl			
				30 37 100	<0.05 <0.05 <0.05	
Spain 1970 50 EC Gordal	1	0.19 ULV, aerial + bait	0.75	0 7 30 88	0.2 0.25 <0.05 <0.05	196-70 As for 314/69
Greece 1984 500EC Konservolia Stilidas	4	0.09 ULV, aerial + bait	1.8	0 7 14 21	0.12 0.23 <0.1 <0.1	5000-84 Olson 1967 0.1 mg/kg
Greece 1988 500 EC Amphissis	3	0.09, ULV, aerial	0.97	0 8	0.16 0.05	0032-88 Olson 1988 0.01 mg/kg
Greece 1988 500 EC Amphissis	4	0.09 ULV, aerial	0.97	0 26	0.16 0.04	0033-88 As for 0032-88
Greece 1988 500 EC Amphissis	3	0.09, ULV aerial	0.97	0 27	0.02 0.01	0034-88 As for 0032-88
Italy 1990 250 EC Coratina	2	0.5 ground, full cover	0.05	0 14 28	1.7 0.92 0.87	0279-90 Ohs 1991 0.01 mg/kg
Italy 1990 250 EC Leccino	2	0.5 ground, full cover	0.05	0 14 28	0.86 0.39 0.26	0712-90 As for 0279-90
Italy 1990 250 EC Nocellara del Belice	2	0.5 ground, full cover	0.05	0 14 28	0.93 0.84 0.36	0713-90 As for 279-90

In the 1968 Spanish trials the spray concentration was 1.5 kg ai/hl which is higher than any reported GAP, but since the trials were ULV at 0.3 kg ai/ha they were evaluated against Italian GAP of 0.25-0.5 kg ai/ha with 2-3 applications and a 28-day PHI. However, trial 381A-68 did not include results at 28 days and was not considered further. The aerial applications in Spain in 1969 and 1970 were not considered to meet any European GAP for aerial application as the 0.15 and 0.19 kg ai/ha rates used are approximately twice the registered Greek and proposed Southern European aerial GAP rate of 0.09 kg ai/ha.

The Greek trials were according to Greek GAP for aerial application (3-5 treatments at 0.09 kg ai/ha with a 21-day PHI) except that in trial 0032-88 samples were taken only at 0 and 8 days.

The Italian trials were with ground applications according to Italian GAP (2-3 treatments at 0.025-0.05 kg ai/hl (0.25-0.5 kg ai/ha) with a 28-day PHI).

One of the Spanish, three of the Greek and the three Italian trials were conducted according to relevant GAP.

Blank values were all <0.01 mg/kg in the 1988 Greek trials and the Italian trials 0712-90 and 0713-90. In trial 0279-90 the blank was 0.23 mg/kg at day 0 and 0.11 mg/kg at days 14 and 28.

A published report of a supervised trial in Italy (Cabras *et al.*, 1993) in which olives were sprayed 3 or 5 times at a rate of 0.2 kg ai/hl (approximately equivalent to 0.075 or 0.1 kg ai/ha) was supplied. Olives were sampled at 0, 11, 20,34 and 54 days after the last treatment and analysed for fenthion, fenthion oxon, and their sulfoxides and sulfones by GLC with a nitrogen-phosphorus detector. Limits of determination were between 0.002 and 0.01 mg/kg. The results were presented as means with standard deviations. The trial did not comply with Italian GAP but reflected the current Greek GAP for ground applications with bait (0.3 kg ai/hl (0.07 kg ai/ha), 21-day PHI, 3-5 applications). As the original data were not supplied, the results were not evaluated further. Table 6 shows the means and standard deviations reported. Table 44 gives the residues in processed olive products.

Rice. GAP for rice in Japan requires 1 or 2 applications of 2% DP at 0.6-0.8 kg ai/ha, PHI 21 days; 50% EC at 0.375-0.75 kg ai/ha, PHI 30 days; 5% GR at 1.5-2.0 kg ai/ha, PHI 45 days, or 40% WP at 0.4-0.75 kg ai/ha, PHI 30 days.

Results of trials in Japan between 1969 and 1978, all approximating GAP, are given in Table 21.

Residues were determined in hulled rice. Three of the trials included analyses of polished rice grains and rice bran.

Total residues of fenthion and its oxidative metabolites were determined by GLC with either an AFID or FPD. The limits of determination were ≤0.001 mg/kg with recoveries of 97% at 0.1 mg/kg and in trial 17/72 91% at 0.02 mg/kg, except in trials 33/79 and 11/71 in which the limits of determination were 0.02 and 0.002 mg/kg and recoveries 90% at 0.25 mg/kg and 89% at 0.02 mg/kg respectively. The plot sizes were not reported.

Table 21. Total fenthion residues found in trials on rice in Japan in 1969, 1971, 1972 and 1978 with DP, EC, and GR formulations.

Year, variety, type[1]	Application	PHI, days	Residues, mg/kg, in hulled rice	Report no.

	Form.	No.	kg ai/ha	kg ai/hl			
1969 Fujiminori Koshiminori Norin juha-chigo, P	DP 2%	1	0.6	-	15 21 30 31 40	<0.001x2 0.009 0.001 0.012 <0.001	18/69 19/69 23/69
		3	0.6	-	20 40 45	<0.001 <0.001 <0.001	
1969 Chuseishin-senbon, P	DP 2%	1	0.6-0.8	-	14 29	0.014 0.01	20/69
	DP 2%	3	0.6-0.8	-	34	<0.001	
1969 Nihonbare Satchiwatari, P	DP 2%	1	0.8	-	7 15 21 30	<0.001 <0.001 <0.001 <0.001	21/69 22/69
	DP 2%	3	0.8	-	15 21	<0.001 <0.001	
1969 Norin juichigo, U	DP 2%	1	0.8	-	15 30	<0.001 <0.001	26/69
	DP 2%	3	0.8	-	40	<0.001	
1969 Norin nijugo, U	DP 2%	1	0.9	-	14 32	0.016 <0.001	25/69
	2%	3	0.9	-	32	<0.001	
1969 Himehanami, P	50 EC	1	0.5	0.05	12 27	0.034 <0.001[2] 0.16[3] 0.018	15/69a 15/69b
	50 EC	3	0.5	0.05	43	<0.001	
1969 Kin nanpu, P	50 EC	1	0.7	0.05	15 30	0.022 0.008	25a/69
	50 EC	3	0.7	0.05	47	<0.001	
1969 Hatasangoku, U	50 EC	1	0.7	0.05	14 28	0.035 <0.001[2] 0.068[3] 0.01	24/69 17/69
	50 EC	3	0.7	0.05	43	<0.001	
1969 Fujiminori, P	50 EC	1	0.5-0.75	0.05	21 40	0.068 <0.001[2] 0.11[3] <0.001	16/69
	50 EC	3	0.5-0.75	0.05	40	<0.001	
1971-2 Harebare (17/72) Sasaminori (11/71)	GR 5%	2	2.0	-	43 56	<0.002 <0.002	17/72 11/71
1978 No variety stated	DP Dust 2%	2	0.8	-	23	<0.024 (residues calculated as total P=O and P=S)	33/79
	Dust	2	0.8	-	23	<0.024 (residues calculated as total P=O and P=S	

[1] P = paddy field rice (rice grown in flooded paddy fields), U = upland rice
[2] polished rice
[3] rice bran

The 1969 trials showed total residues in polished rice from single EC applications of <0.001 mg/kg (three trials) indicating that transfer of residues to the grain was minimal. Residues in rice bran from the same trials were 0.068, 0.11 and 0.16 mg/kg.

Residues were determined in the straw in the 1971-2 and 1978 trials but the results are not shown in Table 21. In trial 17/71 (1971) residues were 0.016 mg/kg at 56 days after two applications of a GR formulation at 2 kg ai/ha and 0.017 mg/kg 37 days after four applications. In trial 17/72 (1972), the total fenthion residue in straw after 4 applications of a GR formulations at 2 kg ai/ha and a 17-day PHI was 0.097 mg/kg. In the 1978 trials with DP formulations, rice straw contained approximately 0.7 mg/kg (P=S + P=O) after two applications at 0.8 kg ai/ha and 23-day PHIs.

Residue data were also supplied from trials in 1994 to support reductions of the PHI fdrom 30 to 21 days for dust formulations and from 45 to 30 days for EC and WP formulations. In most of the trials two applications were made with different formulations: granule and dustable powder, granule and emulsifiable concentrate, or emulsifiable concentrate and dustable powder. Other trials were with two applications of dustable powder. All the trials were according to GAP. Table 22 shows the results.

Residues were determined in the husked rice according to the method of Takino and Kurogochi (1995). The minimum detectable levels reported were 0.004-0.005 mg/kg. Residues were determined as the sum of the thion (P=S) and oxon (P=O) residues. Recoveries of fenthion, its oxon and their sulfoxides and sulfones at 0.1 and 0.2 mg/kg were 85-103%.

Plot sizes were between 15 and 270 sq m on soils described as volcanic ash (Tochigi), alluvial sandy loam (Chiba), clay (Fukui), loam (Mie), diluvial clay loam (Wakayama), Kochi (clay loam), Miyazaki (grey, lowland), and loam (Kagoshima).

Table 22. Total fenthion residues found in rice grains without husk in Japan in 1994 with DP, EC, and GR formulations. All trials with 2 applications.

Variety	Application		PHI, days	Residues, mg/kg[1]	Trial Reference/remarks
	Form.	kg ai/ha			
Hitomebore	GR,DL[2]	1.6, 0.8	21	<0.015	A-1, Tochigi
Koshihikari	GR,DL	1.6, 0.8	20	<0.014,<0.015	A-2, Chiba
Hana-echizen	GR,DL	1.6, 0.8	21	<0.015	A-3, Fukui
Koshikari	GR,DL	1.6, 0.8	21	<0.014, <0.015	A-4, Mie
Hinohikari	GR,DL	1.6, 0.8	21	<0.019	A-5, Wakayama
Koganenishiki	GR,DL	1.6, 0.8	21	<0.015	A-6, Kochi
Hinohikari	GR,DL	1.6, 0.8	21	<0.015	A-7, Miyazaki
Minamihikari	GR,DL	1.6, 0.8	21	<0.015	A-8, Kagoshima
Hitomebore	GR,EC[3]	1.6, 0.75	29	<0.023	B-1, Tochigi, EC 0.05 kg/hl
Koshihikari	GR,EC	1.6, 0.75	29	<0.014, <0.015	B-2, Chiba, EC 0.05 kg/hl
Hana-echizen	GR,EC	1.6, 0.75	30	<0.015	B-3, Fukui, EC 0.05 kg/hl
Koshhikari	GR,EC	1.6, 0.75	30	<0.014, <0.015	B-4, Mie, EC 0.05 kg/hl
Hinohikari	GR,EC	1.6, 0.75	30	<0.019	B-5, Wakayama, EC 0.05 kg/hl
Koganenishiki	GR,EC	1.6, 0.75	30	<0.024	B-6, Kochi, EC 0.05 kg/hl
Hinohikari	GR,EC	1.6, 0.75	30	<0.02	B-7, Miyazaki, EC 0.05 kg/hl
Minamihikari	GR,EC	1.6, 0.75	30	<0.024	B-8, Kagoshima, EC 0.05 kg/hl
Hitomebore	EC,DL[4]	0.75, 0.8	21	<0.028	C-1, Tochigi, EC 0.05 kg/hl

Variety	Application		PHI, days	Residues, mg/kg[1]	Trial Reference/remarks
	Form.	kg ai/ha			
Koshihikari	EC,DL	0.75, 0.8	20	<0.014, <0.015	C-2, Chiba, EC 0.05 kg/hl
Han-echizen	EC,DL	0.75, 0.8	21	<0.015	C-3, Fukui, EC 0.05 kg/hl
Koshihikari	EC,DL	0.75, 0.8	21	<0.014, <0.015	C-4, Mie, EC 0.05 kg/hl
Hinohikari	EC,DL	0.75, 0.8	21	<0.028	C-5, Wakayama, EC 0.05 kg/hl
Koganenishiki	EC,DL	0.75, 0.8	21	<0.025	C-6, Kochi, EC 0.05 kg/hl
Hinohikari	EC,DL	0.75, 0.8	21	<0.024	C-7, Miyazaki, EC 0.05 kg/hl
Minamihikari	EC,DL	0.75, 0.8	21	<0.025	C-8, Kagoshima, EC 0.05 kg/hl
Hitomebore	DL x 2	1.6, 0.8	21	<0.016	D-1, Tochigi, two applications of DP. First application 1.6 kg ai/ha
Koshihikari	DL x 2	0.6	20	<0.014, <0.015	D-2, Chiba, both applications at 0.6 kg ai/ha
Hana-echizen	DL x 2	0.8	21	<0.015	D-3, Fukui, both applications at 0.8 kg ai/ha
Koshihikari	DL x 2	0.6	21	<0.014, <0.015	D-4, Mie, both applications at 0.6 kg ai/ha
Hinohikari	DL x 2	0.6	21	<0.016	D-5, Wakayama, both applications at 0.6 kg ai/ha
Hinohikari	DL x 2	0.8	21	<0.015	D-6, Miyazaki, both applications at 0.8 kg ai/ha
Minamihikari	DL x 2	0.8	21	<0.017	D-7, Kagoshima, both applications at 0.8 kg ai/ha

[1] Sum of thions (P=S) and oxons (P=O)
[2] GR applied 60 days pre-harvest, DL (equivalent to DP) 220-21 days pre-harvest.
[3] GR applied 60 days pre-harvest, EC 29-30 days pre-harvest
[4] EC applied 30 days pre-harvest, DL 20-21 days pre-harvest

Post-harvest disinfestation

Trials to determine residues after post-harvest disinfestation of fruit and vegetables were carries out in Australia, where fenthion has an important use in allowing horticultural products to meet international quarantine requirements.

Fruit flies cause significant damage, are expensive to control and are easily imported in produce. Consequently many countries apply quarantines against them. Treatment to ensure that quarantine requirements are met must be extremely efficacious (providing virtually 100% mortality). The use of ethylene dibromide and methyl bromide as fumigants is being phased out on environmental grounds and irradiation is not widely accepted. Heat and cold treatments can cause physiological damage to many crops. Post-harvest treatments with insecticides provide simple and effective disinfestation without phytotoxicity and fenthion is effective in this role.

Post-harvest disinfestation with fenthion is a registered use in Australia, and that country has requested the establishment of Codex MRLs to cover the use. Data on fruits and vegetables treated post-harvest are shown in Table 23. Because of the nature of the treatment and the commercial requirements of trading treated material, a 0-day PHI is allowed and GAP for quarentine treament is a single flood spray or dip at 0.041 kg ai/hl with no PHI. The trials were in the 1980s (tomatoes 1984; mangoes and capsicums 1986; zucchini 1988; rockmelons and cucumbers 1989).

Table 23. Fenthion residues in fruits and vegetables following a single post-harvest dip or spray with an EC formulation. Trials were in Australia between 1984 and 1989.

Commodity	Rate, kg fenthion/hl	Fenthion residues (mg/kg) at 0, 3, and 7 days after treatment		
		0	3	7
Mango	0.037	1.4, 0.98	0.84, 1.5	0.89, 0.9

fenthion

Commodity	Rate, kg fenthion/hl	Fenthion residues (mg/kg) at 0, 3, and 7 days after treatment		
		0	3	7
Rockmelon	0.043	2.1, 1.5	2.1, 1.5	0.9, 1.3
Cucumber	0.043	1.5, 2.0	1.2, 0.7	0.5, 1.2
Zucchini	0.039	1.0, 1.2	0.06, 0.04	0.01, 0.02
Capsicum	0.038	1.7, 2.3	1.6, 1.5	2.6, 2.1
Tomato	0.042	1.2, 1.3	0.8, 1.1	0.59, 1.1
Mango	0.072[1]	2.2, 1.6	1.6, 1.8	1.3, 1.0
Rockmelon	0.06[1]	1.7, 2.2	1.1, 1.6	1.5, 1.4
Cucumber	0.06[1]	4.2, 4.0	1.6, 1.4	1.1, 1.6
Capsicum	0.069[1]	3.3, 3.0	2.9, 2.8	2.5, 2.5

[1] Excessive concentrations

Residues were extracted with acetone and the acetone extract cleaned up by sweep co-distillation. Fenthion was determined by GLC with an FPD. The method had a limit of determination of 0.01-0.02 mg/kg and determined only fenthion. Recoveries were >80%.

Residues were determined in the whole fruit or vegetable except in mangoes whose peel and pulp were analysed separately and the residue in the whole fruit calculated. In mangoes most of the residue was on the peel (5.7 and 4.8 mg/kg at 0 days, 4.5 and 7.2 mg/kg at 3 days and 3.4 and 3.9 mg/kg at 7 days from 0.037 kg fenthion/hl). In the pulp the corresponding values were 0.21 and 0.06, 0.01 and 0.04, and 0.27 and 0.02 mg/kg.

The residues of fenthion arising from the registered post-harvest uses were generally similar and in the 1-2.5 mg/kg range on the day of treatment. Residues decreased only slowly. Although the treatments were indoors and the extensive formation of fenthion metabolites on the day of treatment may be unlikely, the trials did not conclusively demonstrate that it did not occur.

Animal residues

Residues from use as an ectoparasiticide

Data were supplied on residues in pig and sheep tissues and in cattle tissues and milk after the topical application of fenthion.

Cattle. Registered uses were provided by the sponsor. Dose rates range from 4 to 16 mg/kg bw. A single application is normal practice but redosing is permitted. Withholding periods for edible tissues are 10, 14, 15, 21, 28, 35 or 45 days and for milk 0, 5 or 7 days, depending on the country of registration. In Argentina, Brazil, Canada, Costa Rica, the Dominican Republic, Guatemala, Honduras, Mexico, New Zealand, Nicaragua, Uruguay and the USA the use of fenthion is restricted to non-lactating cattle.

Residues in tissues. Seven trials carried out in the USA from 1965 to 1974 (five back line, one spray and one back rubber. One trial involved two treatments). Dose rates and time intervals (10-45 days) were consistent with the current registered use patterns.

Hereford and Brama steers and females (live weights between about 270 and 420 kg at the beginning of the trial) were slaughtered in groups of 3 at 1, 3, 7, 14 or 28 days after single backline applications of a 2% fenthion pour-on formulation at approximately 6.2 mg ai/kg bw (0.01 oz. ai/100 lbs) (Chemagro, 1965b). Fat, brain, heart, kidneys, liver and muscle were analysed for total fenthion by the method of Anderson and Katague (1965) with a limit of determination of 0.1 mg/kg. The results are shown in Table 24.

Fat contained the highest residues with the maximum value (3.9 mg/kg, 7 days after treatment) found in back fat. By day 28 residues in all fat samples were <0.1 mg/kg. Residues were low in offal, typically <0.1 mg/kg 3 days after treatment, and were all <0.1 mg/kg in muscle after 14 days. treatment.

Table 24. Total fenthion residues in tissues from 15 cattle in the USA in 1965 given a single backline treatment with a 2% fenthion pour-on formulation at 6.3 mg/kg bw (Chemagro, 1965b).

Tissue/organ	Residues, mg/kg, at days after application[1]				
	1	3	7[2]	14	28

Tissue/organ	Residues, mg/kg, at days after application[1]				
	1	3	7[2]	14	28
Brain	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3	<0.1	-
Heart	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3	<0.1	-
Liver	0.2 x 3	<0.1 x 3	<0.1 x 3	<0.1	-
Kidneys	<0.1, 0.1 x 2	<0.1 x 3	<0.1 x 3	<0.1	-
Loin muscle	<01 x 2, 0.4	<0.1 x 2, 0.2	<0.1, 0.1, 0.2	<0.1 x 3	<0.1 x 3
Round muscle	<0.01 x 2, 0.1	<0.1 x 3	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3
Flank muscle	0.1, 0.2, 0.4	<0.1, 0.1, 0.2	<0.1 x 2, 0.1	<0.1 x 3	<0.1 x 3
Omental fat	0.2, 0.8, 1.5	0.3, 0.5, 0.6	0.1, 0.2, 0.3	<0.1 x 2, 0.1	<0.1 x 3
Renal fat	0.3, 0.7, 1.8	0.3, 0.5, 0.6	0.3, 0.5, 2.9	<0.1 x 2, 0.2	<0.1 x 3
Back fat	0.2, 0.8, 1.1	0.1, 0.4, 0.6	0.1, 0.6, 3.9	<0.1 x 3	<0.1 x 3

[1] Control values were <0.01 mg/kg in all tissues
[2] Results after 7 days treated as being after a 10-day withholding period

In a second study 12 cattle (mixed breeds, initial live weights between 300 and 450 kg) were slaughtered in groups of 3 at 1, 3, 7 and 28 days after single backline applications of a 3% pour-on at approximately 9.3 mg ai/kg bw (0.015 oz/100 lbs) (Chemagro, 1968). Brain, heart, fat, kidneys, liver and muscle were analysed for total fenthion residues by the method of Thornton (1967) with a limit of determination of 0.01 mg/kg. The results are shown in Table 25.

Residues were highest after 1, 3, or 7 days, and by day 28 were all <0.1 mg/kg except in two back fat samples (0.12 and 0.13 mg/kg).

Table 25. Total fenthion residues in tissues from 12 cattle given a single backline treatment in the USA in 1968 with a 3% fenthion pour-on formulation at 9.3 mg/kg bw (Chemagro, 1968).

Tissue/organ	Residues, mg/kg, at days after application[1]			
	1	3	7[2]	28
Brain	0.07, 0.02, 0.15	<0.01 x 3	<0.01 x 2, 0.01	<0.01 x 3
Heart	0.1, 0.12, 0.26	<0.02, 0.02, 0.07	0.06, 0.05, 0.11	<0.02 x 3
Liver[3]	0.12, 0.15 x 2	<0.01, 0.01, 0.02	<0.01, 0.01, 0.02	<0.01 x 3
Kidneys	0.07, 0.08, 0.31	0.05, 0.1, 0.02	0.06, 0.08, 0.15	<0.01 x 2, 0.05
Loin muscle	0.06, 0.15, 0.33	0.03, 0.06 x 2	0.03, 0.07, 0.11	<0.01 x 2, 0.02
Round muscle	0.05, 0.15, 0.16	0.02 x 2, 0.03	0.07, 0.1, 0.13	<0.01 x 3
Flank muscle	0.07, 0.16, 0.34	0.03, 0.08, 0.14	0.06, 0.26, 0.31	<0.01 x 2, 0.02
Omental fat	0.11, 0.17, 0.29	0.12, 0.13, 0.18	0.25, 0.29, 0.4	0.02 x 2, 0.03
Renal fat	0.11, 0.18, 0.26	0.31, 0.33, 0.97	0.29, 0.32, 0.54	0.02, 0.03, 0.04
Back fat	0.13, 0.19, 0.25	0.74, 0.87 x 2	0.41, 0.6, 0.84	0.02, 0.12, 0.13

[1] Control values ≤0.01 mg/kg in all tissues except heart (0.02 mg/kg)
[2] Results after 7 days were treated as being after a 10-day withholding period
[3] Samples taken on day 3 analysed 1 day later. Samples taken on days 1 and 7 analysed 4 days later

Two mixed breed, male cattle were treated with 12 ml of a 20% fenthion spot-on formulation in the USA (Chemagro, 1970). They weighed 403 and 427 kg at the start of the trial. The dose administered was 0.084 oz ai/animal, approximately 5.6 and 5.9 mg fenthion/kg bw. The animals were killed after 45 days and residues in brain, heart, liver, kidneys, loin muscle, round muscle, flank muscle, treatment site, omental fat, renal fat and back fat were determined by the method of Thornton (1967). The trial complied with the registered US use pattern of a 5.5-11 mg ai/kg application with a 45-day withholding period.

The samples were analysed in duplicate. All residues were at or below the control values (brain 0.01 mg/kg; heart, liver and kidneys <0.01 mg/kg; muscle and treatment site 0.02 mg/kg; fat 0.05 mg/kg) except one sample of brain at 0.02 mg/kg and one of loin muscle at 0.03 mg/kg.

Two yearling Angus heifers (starting weights 294 and 321 kg) were treated once on the back line with a 20% spot-on formulation at a dose equivalent to 17.7 mg fenthion/kg bw (Cox, 1971). The animals were killed 28 days later and analysed for residues by the method of Thornton (1967). The trial was considered to accord with the registered use patterns of those countries which permit rates up to 16 mg fenthion/kg bw. The results are shown in Table 26.

Table 26. Total fenthion residues in 2 cattle after single back line treatments with a 20% fenthion solution at 17.7 mg/kg bw in the USA (1971) and slaughtered 28 days after treatment (Cox, 1971).

Tissue/organ	Residue, mg/kg
Heart	0.03, 0.06
Liver	0.01, 0.02
Kidneys	0.03, 0.05
Round muscle	0.02, 0.04
Treatment site fat	0.09, 0.47[1]
Non-treatment site back fat	0.09, 0.46[1]

[1] Confirmed by reanalysis

Six mixed-breed yearling heifers were treated twice with a 20% fenthion solution (spot-on back line) at either 11.8 or 17.7 mg fenthion/kg bw (Chemagro, 1974). The rate used for cattle grub control in the USA is 5.5-11 mg fenthion/kg bw. Samples of back fat were taken after 35 days: the second treatment was then given and samples taken after 45 days. The first samples were taken from the left side of the animals near to the site of application and the second from the right side from the equivalent position. Residues were determined by the method of Thornton (1967).

The residues from the low treatment rate were 0.03, 0.01 and 0.03 mg/kg 35 days after the first treatment and 0.07, 0.02 and 0.03 mg/kg 45 days after the second treatment. Those from the high rate were 0.09, 0.03 and 0.04 mg/kg after 35 days and 0.09, <0.01 and 0.06 mg/kg after 45 days.

Since treatments up to 16 mg/kg are allowed in some countries, the dosage rates were considered to accord with registered use patterns. CLICK HERE to continue

HALOXYFOP (193)

IDENTITY

ISO common name: haloxyfop

Chemical name:

IUPAC: (*RS*)-2-[4-[(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionic acid

CA: (±)-2-[4-[[3-chloro-5-trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid

haloxyfop-etotyl (haloxyfop ethoxyethyl ester)

IUPAC: Ethoxyethyl (*RS*)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate

CA: (±)-2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid 2-ethoxyethyl ester

haloxyfop-methyl (haloxyfop methyl ester)

IUPAC: Methyl (*RS*)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate

CA: (±)-2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid methyl ester

haloxyfop-R-methyl (methyl ester of (R)- isomer of haloxyfop)

IUPAC: Methyl (*R*)-2-[4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenoxy]propionate

CA: (+)-2-[4-[[3-chloro-5-(trifluoromethyl)-2-pyridinyl]oxy]phenoxy]propanoic acid methyl ester

CAS No: 87237-48-7 (haloxyfop-etotyl)
069806-40-2 (haloxyfop-methyl)
072619-32-0 (haloxyfop-R-methyl)

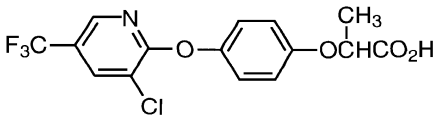
CIPAC No: Numbers have not been assigned

Synonyms: "Gallant" (haloxyfop-etotyl), "Gallant Super" (haloxyfop-R-methyl), "Verdict" (haloxyfop-methyl), "Zelleck", "Eloge", "Bastional", "Mirage"

haloxyfop

Structural formulae: I haloxyfop; II haloxyfop ethoxyethyl ester; III haloxyfop methyl ester; IV haloxyfop-R methyl ester.

I



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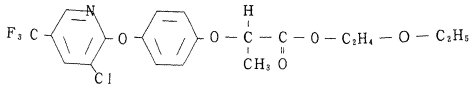

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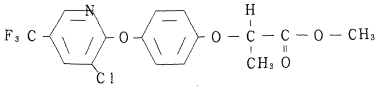

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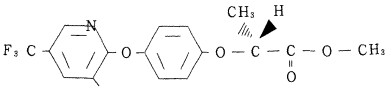


Molecular formula: $C_{15}H_{11}ClF_3NO_4$

haloxyfop-etotyl $C_{19}H_{19}ClF_3NO_5$

haloxyfop-methyl and haloxyfop-R-methyl $C_{16}H_{13}ClF_3NO_4$

Molecular weight: 361.7

haloxyfop-etotyl 433.7

haloxyfop-methyl and haloxyfop-R-methyl 375.5

Physical and chemical properties

haloxyfop-etotyl

Pure compound

Appearance:	white crystalline solid	
Vapour pressure:	1.64×10^{-5} hPa at 20°C	
Melting point:	56-58°C	
Density	1.3489 g/cm^3 at 20°C	
Partition coefficient:	Log P_{ow} 4.33 at 20°C	
Solubility:	Water, mg/l at 20°	0.58 Purified water
		1.91 pH 5.0
		1.28 pH 9.2

Solubility: g/l at 21°C

(contd.)

Hexane	44
Toluene	>1000
Xylene	>1000
Dichloromethane	>1000
Acetone	>1000
Ethyl acetate	>1000
Methanol	233
Propan-2-ol	52

Hydrolysis: Unstable in alkaline conditions

Half-life at 22°C:

pH 5	26 days
pH 7	10 days
pH 9	<1 day

Photolysis: on soil

No degradation over 28 days at 25°C.

in water

First order half-life approximately one month in sterile buffer (pH 5) subjected to artificial light (simulating 40° latitude midday in midsummer)

Technical material

Appearance:	Pale brown solid
Purity:	97.8%
Melting range:	58-61°C
Stability:	No decomposition after 15 days at 70°C; 2% loss after one month at 90°C

haloxyfop-methyl

Pure compound

Appearance:	white crystalline solid
Vapour pressure:	4.9×10^{-7} hPa at 25°C
Melting point:	55-57°C
Density	1.3 g/cm^3 at 20°C(technical material)
Partition coefficient:	Log P_{ow} 3.52 at 20°C

Solubility:

water	9.3 mg/l at 25°C
Acetone	355g/100g solvent at 20°C
Acetonitrile	400g/100g solvent at 20°C
Dichloromethane	300g/100g solvent at 20°C
Xylene	127g/100g solvent at 20°C

Hydrolysis: Unstable in alkaline conditions

Half-life at 25°C:

pH 5	141 days
pH 7	18 days
pH 9	2 hours

Photolysis: on soil

No degradation during 28 days at 25°C

in water

First order half-life approximately one month in sterile buffer (pH 5) subjected to artificial light (simulating 40° latitude midday in midsummer)

Technical material

Appearance:	White crystalline solid
Purity:	99%
Melting range:	55-57°C
Stability:	Haloxyfop-methyl is very stable to heat. No decomposition after 88 hours at 200°C.

haloxyfop-R-methyl

Pure compound

Appearance:	Clear colourless liquid
Vapour pressure:	2.6×10^{-5} hPa at 20°C
Boiling point:	>280°C
Density	1.372 g/cm^3 at 20°C
Partition coefficient:	Log P_{ow} 4.00 at 20°C
Solubility:	water 9.08 mg/l at 20°C, purified water 6.93 mg/l at 20°C, pH 5.0
	acetone, cyclohexanone, dichloromethane, ethanol, ethyl acetate, hexane, isopropyl alcohol, methanol, toluene, xylene >1000g/l at 20 ± 5°C

Hydrolysis: Unstable in alkaline conditions

Half-life at 22°C:

pH 5	161 days
pH 7	16 days
pH 9	<1 day

Photolysis: Not determined

Technical material

Appearance:	Clear brown liquid
Purity:	98.6%-91.7%
Boiling range:	>280°C estimated value >437°C
Stability:	No significant isomerization after one month at 38°C or 50°C, or in contact with metals after one month at 50°C. The assay was above 98% of the initial value in all cases after one month.

Formulations

Haloxyfop-etotyl	EC 104 g/l (acid equivalent)
Haloxyfop-methyl	EC 240 g/l (acid equivalent)
Haloxyfop-R-methyl	EC 104-260 g/l (acid equivalent)

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Animal metabolism studies have been conducted in rats, mice, dogs, monkeys and humans.
Pharmacokinetic and metabolic studies in rats and humans demonstrated that haloxyfop-etotyl and haloxyfop-methyl once absorbed were rapidly hydrolyzed to haloxyfop (parent acid). Haloxyfop is a racemic mixture of (S)- and (R)- enantiomers. In animal systems, haloxyfop-S undergoes rapid and nearly complete inversion to haloxyfop-R.

Rats. In a study on Fischer 344 rats, orally administered ^{14}C-labelled haloxyfop was rapidly absorbed from the gastrointestinal tract (Smith *et al.*, 1982). Both male and female rats excreted over 90% of an oral dose within 5 days. In male rats 70% of the dose was eliminated in the faeces and approximately 20% in the urine. In contrast, female rats eliminated only 20% in the faeces and 70% in the urine. Clearance from the plasma was faster in females, with a half-life of 1.2 days compared with 5.6 days in males. The excreted material was identified as haloxyfop or its conjugates.

The pharmacokinetics of both [^{14}C]haloxyfop-etotyl and [^{14}C]haloxyfop-methyl were evaluated in Fischer 344 rats following oral dosing (Smith *et al*., 1983; Waechter *et al*., 1982). The time course for absorption and elimination of ^{14}C was similar for haloxyfop and these esters. Chromatographic analysis of blood from rats dosed with the esters revealed the presence of haloxyfop at levels to be expected from an equimolar dose of haloxyfop. These findings indicated that haloxyfop and its ethoxyethyl and methyl esters have similar pharmacokinetic profiles and equivalent biological effects may be anticipated since systemic exposure would be to the parent acid, irrespective of whether the acid or an ester was administered.

Mice. A study on $B_6C_3F_1$ mice with ^{14}C-labelled haloxyfop showed no marked sex differences, and a mean half-life of 1.8 days in plasma was established following oral dosing. The faeces was the major route of excretion via the biliary system. As in rats, excretion was as the parent compound and its conjugates (Smith *et al.*, 1984).

Dogs. A pharmacokinetic study was conducted on male beagle dogs following the oral administration of ^{14}C-labelled haloxyfop (Nolan *et al*., 1987). The study showed a biphasic rate of clearance from plasma with half-lives of 1-2 hours and 34 hours. Almost 80% of the excretion was in the faeces, presumably via the biliary system. Excretion was mostly of unchanged haloxyfop.

Monkeys. The pharmacokinetic profile of haloxyfop was also determined in a male cynomolgus monkey following nasogastric administration (Gerbig *et al*., 1985). ^{14}C-labelled haloxyfop was rapidly absorbed from the gastrointestinal tract with peak ^{14}C plasma levels 1-2 hours after dosing. Plasma clearance was biphasic with half-lives of 2.5 hours and 3 days. The urine was the major route of excretion and, as in the other species, excretion was mainly of unchanged haloxyfop and conjugates.

haloxyfop

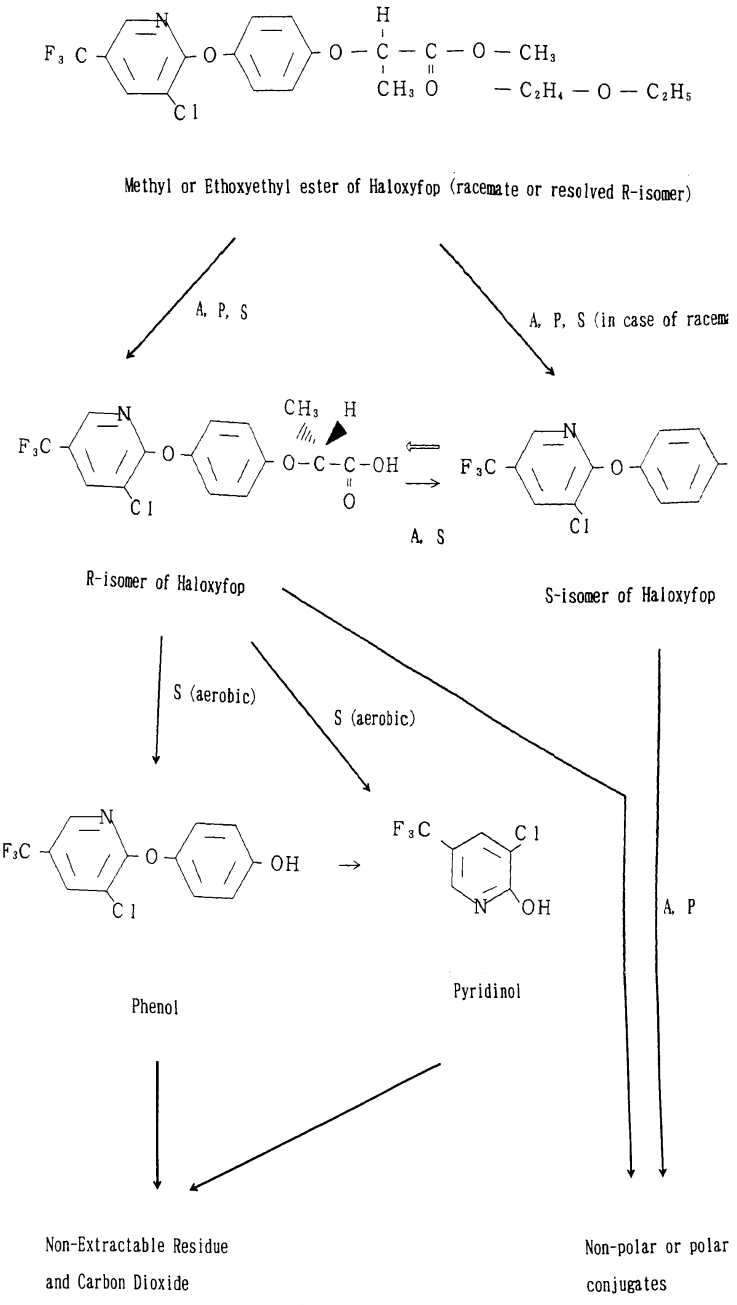
Metabolic pathways are shown in Figure 1.

The following abbreviation are used.

A: in animals	S: in soils under aerobic and anaerobic conditions
P: in plants	S (aerobic): in soils only under aerobic conditions

Phenol: 4-(3-chloro-5-trifluoromethyl-2-pyridyloxy)phenol
Pyridinol: 3-chloro-5-trifluoromethylpyridin-2-ol

Figure 1. Metabolic pathways of haloxyfop in plants, animals and soils.



haloxyfop

Humans. The pharmacokinetics of haloxyfop, haloxyfop-etotyl and haloxyfop-methyl were examined in male volunteers by oral and dermal routes (Nolan, 1985: Nolan *et al*., 1985). The sodium salt of haloxyfop was rapidly absorbed following an oral dose of 0.2 mg/kg bw. One excretion half-life was about 6 days. As in the male monkey and female rat excretion was mostly in the urine and, as in all other species, as unchanged haloxyfop or its conjugates; no metabolic breakdown was apparent (Nolan, 1985). In male humans, dermal absorption of haloxyfop-methyl was slow and minimal. Only 3% of a topically applied dose was absorbed (Nolan, 1985).

In a separate study on humans, formulated haloxyfop-etotyl herbicide containing 12.5% of active ingredient was applied to the forearm of male volunteers (Nolan *et al*., 1985). Only 1.1% of the applied ester was absorbed.

The disposition of haloxyfop in the volunteers given haloxyfop-etotyl (i.e. its clearance from plasma and excretion in the urine) was indistinguishable from its previously reported fate in volunteers given either a single oral dose of haloxyfop or a single dermal dose of haloxyfop-methyl. This indicated that haloxyfop-etotyl was rapidly hydrolyzed to the parent acid and that, once absorbed, its fate was independent of whether haloxyfop or its ethoxyethyl ester had been administered.

Inversion of haloxyfop-S to haloxyfop-R in animals. 2-Arylpropionates are known to undergo stereochemical inversion in several animal species (Wecher *et al*., 1974). A study on rats to determine the stereochemical inversion of haloxyfop was carried out by Bartels and Smith (1989). Groups of Fischer 344 rats, four per sex, were gavaged with approximately 11 mg/kg bw of racemic [*phenyl*-^{14}C]haloxyfop. Urine and faeces samples were analysed for haloxyfop-R. The results showed that haloxyfop-S undergoes rapid and nearly complete inversion to haloxyfop-R. Nearly all of the haloxyfop recovered from the urine and faeces was haloxyfop-R.

Plant metabolism

The fate and metabolism of various esters of haloxyfop have been studied in whole plants, leaves and tissues in a range of plant types covering sugar beet, oilseed rape, cabbages, potatoes, cotton, the legumes soya bean and white dry bean, peanuts and several gramineous species. There is rapid absorption of the esters into treated leaves after application with subsequent hydrolysis to the acid. Isomerization does not occur in plant systems and only haloxyfop-R has herbicidal activity.

Early metabolic fate

Studies of metabolism during the first week after treatment have been carried out on several species: rapid ester hydrolysis and translocation were observed (Bauriedel and Miller, 1981; Buhler *et al*., 1985). Aqueous solutions of [^{14}C]haloxyfop as its n-butyl ester, methyl ester, ethoxyethyl ester or tri-isopropanolamine salt were applied to soya bean leaf surfaces in the greenhouse (Bauriedel and Miller, 1982). Metabolism and translocation were studied up to 8 days after application. The plants were harvested at intervals, separated into treated leaves and untreated remainder, and washed or extracted. The determination of radioactivity and characterization of metabolites were by LSC and chromatographic techniques respectively. The results indicate that the three esters and amine salt of haloxyfop are rapidly absorbed into the leaves after application. Subsequently the esters are hydrolyzed to haloxyfop in the treated leaves, then metabolized to polar metabolites or translocated to the untreated parts as shown in Tables 1 and 2.

Table 1. Distribution of radioactivity in extracts of treated soya bean leaves as determined by HPLC and LSC.

Days after treatment	Ester applied	% of extracted radioactivity		
		Polar fraction	Haloxyfop	Ester of haloxyfop
2	Methyl	34	66	0
	n-Butyl	29	60	11
	Ethoxyethyl	25	58	17
4	Methyl	52	48	0
	n-Butyl	51	43	6
	Ethoxyethyl	52	39	9
8	Methyl	58	40	2
	n-Butyl	62	38	0
	Ethoxyethyl	65	34	1

Table 2. Distribution of radioactivity in extracts of the untreated portions of soya bean plants as determined by HPLC and LSC.

Days after treatment	Ester applied	% of extracted radioactivity		
		Polar fraction	Haloxyfop	Ester of haloxyfop
2	Methyl	17	83	0
	n-Butyl	18	82	0
	Ethoxyethyl	22	78	0
4	Methyl	28	72	0
	n-Butyl	27	73	0
	Ethoxyethyl	25	75	0
8	Methyl	36	64	0
	n-Butyl	39	61	0
	Ethoxyethyl	35	65	0

The polar fractions of the untreated portions of the plants were subjected to mild alkaline hydrolysis (9-ml aliquots of aqueous concentrates were made basic with 1 ml 10N NaOH and heated at 50°C for 2 hours). A proportion of the polar metabolites was converted to free haloxyfop, indicating that the polar fraction consists in part of conjugates of the acid. The equivalence of phenyl- and pyridyl-labelled haloxyfop demonstrated that the ether linkage remained intact.

Long-term fate

Cotton. Aqueous solutions of formulated [*phenyl*-^{14}C]haloxyfop butyl ester were applied to plots of immature, field-grown cotton 32 days after planting by a shrouded plot sprayer, at a rate equivalent to 0.56 kg/ha (Stafford and Miller, 1983). Samples of lint and seed were taken at normal harvest 78 and 105 days after application, together with the remainder of the plant and soil at the last sampling. Oil was extracted from the seed with hexane and all plant materials were extracted with aqueous acetonitrile. The total radioactivity was determined by combustion and LSC and, in extracts, by LSC. Qualitative analyses of the various extracts were by HPLC and GC-MS-RAM. The extracts were also subjected to alkaline hydrolysis or lipase action to determine the nature of the fractionated components.

The concentration of ^{14}C in mature cotton seed was 0.78 mg/kg haloxyfop equivalent 78 days after application and 0.20 mg/kg at 105 days. Residues in cotton lint were 0.19 mg/kg and 0.04 mg/kg at 78 and 105 days after application respectively. Field trash and soil (top 4 cm) at 105 days after application contained 1.09 and 0.73 mg/kg respectively.

Enzymatic or alkaline hydrolysis of the oil (which contained 26 and 55% of the total radioactivity 78 and 105 days after application respectively) indicated that the major product (>91%) was haloxyfop, present as triglyceride conjugates. The radioactivity remaining in the seed coat was mainly from polar conjugates which released haloxyfop under mild alkaline hydrolysis. The major radioactive component in the lint (88%) was free haloxyfop, whilst that in field trash was either free haloxyfop or its polar metabolites.

Sugar beet. Sugar beets at the 6-inch stage of growth were treated with aqueous solutions of (*phenyl*-^{14}C]haloxyfop as the methyl ester at the rate of 0.28 kg acid equivalent per ha, 104 days before normal commercial harvest (Yackovich and Miller, 1984). Samples of mature beet were harvested and separated into tops and roots. The total radiolabelled residues in the samples were determined by combustion and LSC, with a detection limit of 0.004 mg/kg haloxyfop equivalents. Samples were extracted with 50% aqueous acetonitrile and residues in the extracts were identified by HPLC. Residue levels were very low, averaging 0.01 mg/kg in the roots and 0.04 mg/kg in the green leafy portions. Most of the radioactivity (88% of that in the roots and 83% in the tops) was extractable with aqueous acetonitrile, and HPLC analysis indicated that most of the residue (80% roots and 72% tops) was present as free haloxyfop.

Peanut plants. Aqueous solutions of formulated [*phenyl*-^{14}C]haloxyfop-methyl were applied pre-blossom to immature peanut plants(3-4 vines, 5-7 inches long) 113 days before the normal commercial harvest, at a rate equivalent to 0.28 kg/ha acid equivalent (Yackovich and Miller, 1985a). Samples of peanuts, peanut shells and vines were analysed for total radioactivity by combustion and LSC with a determination limit of 0.004 mg/kg as haloxyfop equivalent. Oil was extracted from peanuts with hexane and the remaining cake extracted with 50% aqueous acetonitrile. Qualitative analysis of the extracts was by HPLC, with alkaline hydrolysis of the peanut oil to characterize the non-polar conjugates.

The residues at harvest averaged 0.04 mg/kg in peanuts, 0.07 mg/kg in shells and 0.01 mg/kg in vines. The residue in the extracted oil was 0.06 mg/kg, indicating a 1.5-fold concentration. All the radioactive material in the oil could be hydrolyzed to free haloxyfop with alkali. The remaining meal contained residues of 0.032 mg/kg, 90% of which was extractable by acetonitrile and was mainly free haloxyfop.

Soya beans. Aqueous solutions of a formulated [^{14}C]phenyl-labelled butyl ester of haloxyfop were applied to plots of soya bean plants, either pre-blossom (89 days pre-harvest) or post-blossom (61 days pre-harvest). Additional plots were treated post-blossom with aqueous solutions of formulated [^{14}C]pyridinol-labelled haloxyfop at a rate equivalent to 0.56 kg/ha acid (Yackovich and Miller, 1983). Samples of either whole green plant or new (i.e. post-application) foliage were taken from plants which had had the highest rate pre-blossom treatment 14 days after application. Samples of mature plants were also taken at the normal commercial harvest, air-dried indoors for a week and the beans separated from the straw. The total radioactivity was determined by combustion and LSC or direct LSC of extracts, with a limit of detection of 0.01 mg/kg haloxyfop equivalents. Oil was extracted with hexane and the extract hydrolysed with lipase to determine the nature of the residue. Qualitative analysis of the various extracts was by HPLC and GC-MS-RAM techniques. Mild alkali was used to hydrolyse the extractable polar conjugates.

The total radioactivity in the various plant tissues increased with higher application rate and later timing of application. Levels from post-blossom application in straw were approximately twice,

and in beans four times, those from pre-blossom treatment. The residues in the oil were equivalent to those in the beans, demonstrating that no concentration occurred during extraction. More than 90% of the residue in immature plants 14 days after application was extractable with acetonitrile and comprised approximately one-third free haloxyfop acid and two-thirds polar conjugates. The latter yielded haloxyfop under alkaline hydrolysis. Approximately 5% of the residue present in the whole plant samples was identified as the butyl ester, whilst the new growth contained only haloxyfop or its polar conjugates.

The residues in soya beans at harvest were shown to be extractable into hexane (average 18%) or acetonitrile (average 77%). All the radioactivity from the non-polar conjugates in the hexane extract of the oil was released as free haloxyfop by lipolysis. The acetonitrile extract of the defatted meal contained about 75% of the radioactivity as free haloxyfop and 25% as polar conjugates which gave rise to haloxyfop under alkaline hydrolysis.

More than 93% of the residue in the straw was extractable with acetonitrile and comprised about two-thirds free haloxyfop and one-third polar conjugates which gave rise to haloxyfop under alkaline hydrolysis.

Throughout the study, no differences were apparent in either the level or the nature of the residues from the phenyl- and pyridinol-labelled material and hence no evidence of ring cleavage.

Rape. Aqueous solutions of formulated [*phenyl*-^{14}C]haloxyfop-methyl were applied to immature oilseed rape at a rate equivalent to 0.14 kg/ha acid (Yackovich and Miller, 1985b). Nearly mature rape plant samples were taken and air-dried in a greenhouse before separation into seed and plant remainder (trash). The total ^{14}C in the various fractions was determined by combustion and LSC and corrected for the weight lost on drying. Rape seed oil was extracted with hexane and an aliquot subjected to mild alkaline hydrolysis. The defatted cake was extracted with 50% aqueous acetonitrile and the various extracts analysed by LSC and HPLC. The residual radioactivity was 0.92, 0.52, 1.1 and 1.31 mg/kg haloxyfop equivalents in the seed, oil, cake and trash respectively. The residues in the oil were a very complex mixture of non-polar lipids, which under mild alkaline hydrolysis yielded free haloxyfop. The ^{14}C remaining in the meal after extraction of the oil was mainly in free haloxyfop.

Summary

The experiments demonstrated rapid absorption and assimilation of the esters into treated leaves after application. Subsequent hydrolysis to the parent acid occurred at slightly different rates, in the order methyl > butyl > ethoxyethyl. Since the fate of the three esters is essentially similar, data from studies of the butyl ester are relevant. No data on plant metabolism studies with the R-isomer of haloxyfop were provided, but are not thought to be necessary since the data on racemic haloxyfop demonstrated that the major metabolites are free haloxyfop and its conjugates, all of which are included in residue analysis.

Conjugation of the parent acid to form more polar components, probably glycosides, occurred within treated leaf tissue, with different patterns of conjugates exhibited by different species. The conjugates yield haloxyfop under mild alkaline hydrolysis.

The main compound translocated to untreated aerial parts and roots was shown to be haloxyfop, but whether the polar conjugates are translocated or formed *in situ* from translocated acid was not established.

Crop components with a high oil content, e.g. rape seed, cotton seed, soya beans and peanuts, accumulated haloxyfop as non-polar triglyceride conjugates, which were hydrolysed to free haloxyfop by lipase or alkali. Defatted seed residues, e.g. meal, seed coats, cotton lint or peanut shells, contained

either free haloxyfop or polar conjugates. The aqueous acetonitrile extraction procedures used in most of the studies where a mass balance of a sample was attempted indicated that a small proportion of the haloxyfop residue was unextractable.

Herbicidal activity. In soil and mammalian systems rapid hydrolysis of esters to free haloxyfop is followed by conversion of the (*S*)- to the (*R*)- isomer, but this conversion does not occur in plants (Gerwich *et al*., 1988). In a study with known mixtures of (*R*)- and (*S*)-haloxyfop-methyl applied to annual grasses, samples enriched with the (*S*)- isomer were found to be less herbicidally active than the (*R*)- isomer in laboratory petri dish evaluations. The pure (*S*)- isomer was estimated by regression to have 1/1000 or less of the activity of the (*R*)- isomer. However, the (*S*)- and (*R*)- isomers were equally active following pre-emergence soil application, and subsequent isolation of treated soil indicated inversion of the (*S*)- to the (*R*)- isomer within seven days. These results were confirmed in field trials. The conclusion that the (*S*)- isomer is herbicidally inactive is also supported by the observation that only half the foliar application rate of haloxyfop-R formulations is needed compared with racemic formulations to obtain the same degree of efficacy. The inability of plants to isomerize enantiomers has also been demonstrated for other aryloxyphenoxypropionate herbicides, e.g. diclofop, fluazifop and quizalofop (Sakata *et al*., 1985).

Environmental fate in soil

The degradation of haloxyfop has been extensively studied under laboratory and field conditions. Recent studies have mainly been with haloxyfop-R-methyl, but are valid for evaluating the environmental fate of other esters and of racemic haloxyfop since ester hydrolysis and stereochemical inversion occur rapidly in soil.

Aerobic degradation. The degradation of haloxyfop-R methyl was investigated in four soils (Hale and Trigg, 1994). Three UK soils (Marcham sandy clay loam, Marcham loamy sand and Highworth loamy clay) and a standard German soil (Speyer 2.2 sandy loam) were adjusted to 40% of their moisture holding capacities with water in biometer flasks. The soils were then treated with haloxyfop-R methyl at a rate equivalent to 104 g acid/ha and the flasks connected to a low pressure oxygen supply and CO_2 trap and maintained at 20°C in the dark for periods up to 182 days. Samples taken at intervals were extracted sequentially with three organic solvent mixtures and purified for analysis by HPLC. Selected samples were also analysed by TLC to confirm the results. The amount of $^{14}CO_2$ evolved during the degradation was also determined.

The methyl ester was hydrolysed rapidly to haloxyfop in all four soils with only 1.3-5.0% of the applied radioactivity (AR) remaining as ester 1 day after treatment, when maximum levels of the acid (72.6-90.7% AR) were observed. Thereafter the acid was degraded to 4-(3-chloro-5-trifluoromethyl-2-pyridyloxyphenol (hereafter referred to as as the phenol) which was in turn degraded to 3-chloro-5-trifluoromethylpyridin-2-ol (the pyridinol). The phenol reached a mean maximum of 7.0-12.6% AR between 3 and 14 days after treatment, depending on the soil. The maximum levels of the pyridinol ranged between 35.5 and 52.4% AR and were observed at 91 days after treatment. Three further unidentified metabolites were observed, but only one of these exceeded 1% AR: it was present at levels between 2.0% and 9.3% AR (mean) at 182 days after treatment.

The production of $^{14}CO_2$ was slow during the first 28 days of the incubation, but 91 days after treatment 2-3.3% of the applied radioactivity was present as $^{14}CO_2$ in the three UK soils, with a mean of 19.6% AR in the Speyer 2.2 soil. These levels increased to 6.5-11.2% AR in the UK soils and 24.0% AR (mean) in the Speyer 2.2 soil after 182 days. The levels of unextractable residues increased throughout the incubation period to reach a maximum of 23.3-34.7% AR 182 days after treatment. The mass balance for all the soil samples ranged from 83.5 to 103.9% AR (mean 94.0%, standard deviation 5.4).

Half-lives of haloxyfop acid ranged from 9 days in the two Marcham soils to 20 days in the Speyer 2.2 sandy loam. The mass balances are shown in Table 3.

Table 3. Mass balances for the aerobic degradation of haloxyfop-R-methyl in 4 soils.

Fraction	% AR at days after treatment							
	0	1	3	7	14	28	91	182
Haloxyfop-R-methyl	70-83	1-4	0.5-2	0-2	0-8	0-3	0-1	0.4-0.5
CO_2[1]	0	0	0	0-0.1	0.1-0.8	0.5-3	2.5-19.5	6.5-24
Haloxyfop-R	6-18	73-91	61-82	19-56	21-40	18-28	9-15	6-10
Pyridinol	0	0.5-3	1-6	5-14	14-30	23-35	36-53	18-46
Phenol	0-6	2-6	4-12	4-12	6-13	2-7	0.5-4	1-3
Unextractable	0.4-1	1-7	3-17	6-29	11-30	14-33	22-35	23-35
Total	92-94	100-103	85-99	90-99	86-101	87-91	94-101	97-98

[1] Other volatiles were not collected

Anaerobic degradation. The decomposition of the methyl ester of haloxyfop in soil under anaerobic conditions was studied in two soils (from Mississippi and Illinois, USA) at a temperature of 25°C and a concentration of 0.5 mg/kg (Swann and Hertel, J.A. 1983). The ester was hydrolysed very rapidly (half-life <1 day) to haloxyfop. Haloxyfop once formed showed no apparent degradation after 300 days of incubation.

Stereochemical inversion. The aerobic degradation of the methyl esters of racemic haloxyfop, haloxyfop-R, and haloxyfop-S were investigated in Catlin silt loam, Commerce silt loam and Cecil sandy loam soils with specific regard to the stereochemical inversion process (Racke, 1990). The soils were treated with the [3,4,5,6-^{14}C]pyridyl esters at 0.5-0.59 mg/kg and incubated at 26°C for 6 or 12 days. During the incubation period, $^{14}C0_2$ production was monitored with a sodium hydroxide trap. After the incubation soil samples were extracted with a mixture of methyl *tert*-butyl ether (MTBE) and 1.5 M phosphoric acid. All the methyl esters were converted in nearly quantitative yields to a mixture of unextractable ^{14}C and the (*R*)- and (*S*)- isomers of haloxyfop acid. The stereochemical inversion, which followed ester hydrolysis, resulted in the preferential formation of the (*R*)- isomer of haloxyfop from both the racemate and the (*S*)- isomer. It was concluded that the inversion was mediated by micro-organisms, because it did not occur in sterilized soil and was slow at a high application rate and low incubation temperature. The results found with the Catlin soil are shown in Table 4.

Table 4. Recovery and distribution of ^{14}C from Catlin loam soil treated with the mehyl ester of racemic haloxyfop, haloxyfop-R or haloxyfop-S after 6 or 12 days of incubation.

Ester of	% of applied ^{14}C							R/S ratio
	$^{14}CO_2$	Acid phase	MTBE phase	Haloxyfop (*R*)-	(*S*)-	Unextractable	Total[1]	
6 days								
Racemic haloxyfop	0.38	1.62	90.7	68.6	11.8	7.86	100.6	5.81
Haloxyfop-R	0.27	1.66	92.2	83.8	4.5	8.14	102.2	18.6
Haloxyfop-S	0.18	1.92	90.9	71.9	12.4	8.93	101.9	5.79
12 days								
Racemic haloxyfop	0.41	1.92	85.3	77.3	7.35	12.8	100.4	10.51
Haloxyfop-R	0.08	1.48	88.05	82.9	3.7	11.9	101.5	22.41
Haloxyfop-S	0.15	1.89	87.6	70.9	11.4	13.09	102.7	6.22

[1] Sum of CO_2, acid phase, MTBE [methyl *tert*-butyl ether] phase and unextractable

Field studies. The behaviour of formulated haloxyfop-R-methyl has been studied in lysimeter experiments (Yon, 1993). Two sandy soil lysimeters (68% sand, 25% silt, 1.5% organic carbon were sown with sugar beet in April 1989 and treated with labelled haloxyfop-R-methyl at rates equivalent to 112g and 212g ai/ha in the following June. Leachate was collected throughout the experiment and analysed for the total radioactivity. In total, 0.29-0.71% of the applied radioactivity was found in 956-960 l of leachate. Chromatographic analysis showed that haloxyfop-methyl, haloxyfop acid and the pyridinol were all absent. The radioactive component of the leachate consisted almost entirely of a polar unknown in concentrations of 0.03-0.15 ì g/l haloxyfop-methyl equivalents. Soil samples (0-10 cm) were taken from both lysimeters at the end of the first growing season and analysed for total radioactivity after combustion: 39-58% of the applied radioactivity was still present in the top 10 cm. At the end of the experiment soil samples taken to a depth of 1.2 m still contained 25-39% of the applied radioactivity and the majority of this (24-33%) was in the top 30 cm. Less than 1% of the radioactivity had moved to depths greater than 60 cm. Extraction and chromatographic analysis of the 0-10 cm and 10-20 cm horizons showed that both haloxyfop-methyl and haloxyfop were below the detection limit for the GC-MS determination (0.09 ì g/kg). The pyridinol was present at 0.27-1.9 ì g/kg. The total radioactivity in the plants at harvest was 0.01-1.0% of that applied.

Environmental fate in water/sediment systems

The degradation of [*pyridyl*-^{14}C]haloxyfop-etotyl in aerobic ditch waters and their associated sediments (silty clay loam and sandy loam) were studied by Yon and Cresswell (1990) over a period of 26 weeks. Samples were maintained at 16-25°C in the dark and the waters kept aerobic by drawing air through them continuously. The mean recoveries of radioactivity for the silty clay loam and sandy loam were 93.9% and 94.6% respectively. Immediately after treatment of the sediment/water systems most of the radioactivity was in the water, with maximum levels reached 3 and 7 days after application of 78.5% and 79.3% in the silty clay loam and sandy loam respectively. These decreased steadily to 27.7% and 29.8% (after 26 and 21 weeks respectively) with a concomitant increase in the radioactivity associated with the sediment. Carbon dioxide production reached 3.0% and 4.9% and unextractable residues in the soil 3.2% and 4.6% respectively after 26 weeks.

Chromatographic analysis of the water samples and sediment extracts showed that the ester was rapidly hydrolyzed to haloxyfop acid, the concentrations of which were highest after 1 week and then decreased exponentially. At the same time the concentration of the pyridinol increased for 2-4

weeks and then decreased steadily.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Variations of a basic analytical method have been developed for high-moisture low-fat crops, low-moisture high-fat crops and products of animal origin. The analytical procedure constists in extraction and hydrolysis of the ester with alkaline methanol, partitioning into an acid organic phase, alkaline aqueous extraction, acid organic extraction, derivatization to produce the methyl or butyl ester, and column clean-up. In the most used method 10 g of homogenized sample, 1 ml of 20% sodium hydroxide solution and 50 ml methanol are shaken for 2 hours or overnight, when esters or conjugates are hydrolyzed to produce free haloxyfop acid. After centrifugation at 2000 rpm for several minutes, an aliquot of the supernatant is acidified with sulfuric acid and partitioned with an organic solvent such as ethyl ether, toluene or dichloromethane. The organic layer is then partitioned with aqueous sodium bicarbonate, which is acidified again and extracted with a solvent such as ethyl ether. The organic solvent is evaporated and the haloxyfop converted to its butyl or methyl ester by reaction with butanol and sulfuric acid at 100°C for 30 minutes, boron trifluoride and methanol on a steam bath for 2 minutes, or diazomethane. Further clean-up of the sample is achieved on a Florisil column before quantification by gas chromatography with an electron-capture detector. In some cases a silica gel column clean-up or treatment with potassium permanganate is applied before derivatization.

The limits of determination are normally between 0.01 and 0.05 mg/kg.

Stability of pesticide residues in stored analytical samples

The stability of haloxyfop residues in soya beans, green peas and cabbage stored under frozen conditions has been studied (Gardner, 1983a; Hastings and Butcher, 1993a,b). Samples were fortified with haloxyfop-methyl (soya beans) or haloxyfop (green peas and cabbage) at 0.05-0.20 mg/kg and stored deep frozen (<-16°C or -20°C) until analysis after 16-17 months. No losses were found in any of the studies. It was concluded that haloxyfop is stable during storage under frozen conditions and this conclusion was supported by other metabolic studies.

Residue definition

Plant metabolism studies showed that esters of haloxyfop are rapidly metabolized to haloxyfop acid at the treated site and translocated to other parts of the plant. Haloxyfop is further metabolized in some plants to conjugated products. In high-fat crops such as rape seed, cotton seed, soya beans and peanuts, haloxyfop accumulated as non-polar triglyceride conjugates. In animals, esters of haloxyfop are again rapidly hydrolyzed and excreted as haloxyfop or its conjugates in the urine or faeces. Esters and polar and non-polar conjugates of haloxyfop are easily hydrolyzed to haloxyfop under mild alkaline conditions. No other major metabolites have been found. It is concluded that residues should be defined as the sum of haloxyfop esters, haloxyfop and its conjugates, expressed as haloxyfop.

USE PATTERN

Haloxyfop has been developed as a selective herbicide for the control of grass weeds in broad leaf crops. The first formulations were based on either the ethoxyethyl or methyl ester of racemic haloxyfop. Once applied to plants, the esters are rapidly hydrolysed to the acid which is herbicidally active. As it has been demonstrated that it is the (*R*)- isomer of haloxyfop which is herbicidally active, with essentially no activity associated with the (*S*)- isomer, a resolved methyl ester has been developed which is approximately 98% (*R*)- isomer. Formulations containing haloxyfop ethoxyethyl ester (haloxyfop-etotyl) have been developed primarily for the European, Middle East/African regions and Australia. Formulations of haloxyfop-methyl were developed mainly for the North and South American regions. Haloxyfop-R-methyl has been developed for world-wide use and will gradually replace the racemates. Registered use patterns are shown in Tables 5-12, where application rates are expressed as free haloxyfop acid equivalents.

The following abbreviations are used in the Tables.

Active ingredient	
SR:	racemic haloxyfop
R:	resolved (*R*)- isomer of haloxyfop
Me:	methyl ester
EE:	ethoxyethyl ester
Bt:	butyl ester
Application method	
Aer:	aerial
Ap:	broadcast
Gr:	directed at ground below trees or vines
PHI	
BF:	before fruit appears
CC:	up to closing of canopy
ET:	up to early tillering
GC75%:	up to 75% ground cover
HC40 or HC60:	up to 40 or 60 cm height of crop
PE:	application after weed emergence
PE 2-4, PE 3-5 or PE 4-6:	application after weed emergence with weeds at 2-4, 3-5 or 4-6 leaf stage respectively
ST:	to start of tillering

Table 5. Registered uses of haloxyfop on fruit. All single applications of EC.

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
Apples	Hungary	R-Me	Gr	0.042-0.21	0.014-0.1	90
	Romania	R-Me	Gr	0.16	0.052-0.078	PE
Berry fruit	Poland	R-Me	Gr	0.078-0.16	0.02-0.078	CC
	Romania	R-Me	Gr	0.16	0.052-0.078	PE
Citrus	Argentina	SR-Me	Gr	0.084-0.3	0.056-0.3	PE 2-4
	Bolivia	SR-Me	Gr	0.06-0.084	0.04-0.084	PE 2-4
	Paraguay	SR-Me	Gr	0.072-0.18	0.048-0.18	PE 2-4
	Peru	SR-Me	Gr	0.11-0.15	0.028-0.038	PE 2-4
Grapes	Argentina	SR-Me	Gr	0.084-0.3	0.056-0.3	PE 2-4
	Bolivia	SR-Me	Gr	0.06-0.084	0.04-0.084	PE 2-4
	Czech repub.	R-Me	Gr	0.052-0.16	0.013-0.078	CC
	France	R-Me	Gr	0.078-0.31	0.02-0.16	ET

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
	France	SR-EE	Gr	0.16-0.62	0.039-0.31	ET
	Hungary	R-Me	Gr	0.042-0.21	0.014-0.1	90
	Paraguay	SR-Me	Gr	0.072-0.18	0.048-0.18	PE 2-4
	Peru	SR-Me	Gr	0.11-0.15	0.028-0.038	PE 2-4
	Romania	R-Me	Gr	0.16	0.052-0.078	PE
	Slovakia	R-Me	Gr	0.052-0.16	0.013-0.078	CC
	South Africa	SR-EE	Gr	0.1-0.31	0.035-0.16	PE 4-6
Orchards	Australia	R-Me	Gr	0.10-0.21	0.069-0.42	ET
	Australia	R-Me	Aer	0.10-0.21	>0.35	BF
	Australia	SR-EE	Gr	0.21-0.83	0.14-1.7	ET
	Australia	SR-EE	Aer	0.21-0.83	>0.69	BF
	Czech repub.	R-Me	Gr	0.052-0.16	0.013-0.078	CC
	Poland	R-Me	Gr	0.078-0.13	0.02-0.065	CC
	Slovakia	R-Me	Gr	0.052-0.16	0.013-0.078	CC
Pome fruit	Argentina	SR-Me	Gr	0.084-0.3	0.056-0.3	PE 2-4
	Bolivia	SR-Me	Gr	0.06-0.084	0.04-0.084	PE 2-4
	Paraguay	SR-Me	Gr	0.072-0.18	0.048-0.18	PE 2-4
	South Africa	SR-EE	Gr	0.1-0.31	0.035-0.16	PE 4-6
Stone fruit	Argentina	SR-Me	Gr	0.084-0.3	0.056-0.3	PE 2-4
	Bolivia	SR-Me	Gr	0.06-0.084	0.04-0.084	PE 2-4
	Paraguay	SR-Me	Gr	0.072-0.18	0.048-0.18	PE 2-4
	South Africa	SR-EE	Gr	0.1-0.31	0.035-0.16	PE 4-6

Table 6. Registered uses of haloxyfop on vegetables (except sugar beet and legumes). All single EC applications.

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
Cabbage	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	120
Carrots	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	60
	Uzbekistan	R-Me	Ap	0.1-0.21	0.021-0.069	PE 5
Garlic	Spain	SR-EE	Ap	0.1-0.21	0.026-0.1	PE 2-4
Onions	Argentina	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Argentina	SR-Me	Aer	0.084-0.3	0.17-2	PE 2-4
	Chile	R-Me	Ap	0.03-0.15	0.02-0.15	30
	Chile	SR-Me	Ap	0.24-0.3	0.16-0.3	30
	Hungary	R-Me	Ap	0.042-0.21	0.014-0.1	54
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	60
	Spain	SR-EE	Ap	0.1-0.21	0.026-0.1	PE 2-4
	Uzbekistan	R-Me	Ap	0.1-0.21	0.021-0.069	PE
Potatoes	Argentina	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Argentina	SR-Me	Aer	0.084-0.3	0.17-2	PE 2-4

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
	Bolivia	SR-Me	Ap	0.06-0.084	0.04-0.084	PE 2-4
	Bolivia	SR-Me	Aer	0.06-0.084	0.12-0.56	PE 2-4
	Czech repub.	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Ireland	SR-EE	Ap	0.21	0.052-0.1	HC 60
	Hungary	R-Me	Ap	0.042-0.21	0.014-0.1	60
	Paraguay	SR-Me	Ap	0.072-0.18	0.048-0.18	PE 2-4
	Paraguay	SR-Me	Aer	0.072-0.18	0.14-1.2	PE 2-4
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	120
	Romania	R-Me	Ap	0.16	0.052-0.078	HC 40
	Slovakia	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Spain	SR-EE	Ap	0.1-0.42	0.026-0.21	PE 2-4
	Uruguay	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Uruguay	SR-Me	Aer	0.084-0.3	0.17-2.0	PE 2-4
	Uzbekistan	R-Me	Ap	0.1-0.21	0.021-0.069	PE
Tomatoes	Hungary	R-Me	Ap	0.042-0.21	0.014-0.1	21
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	60
Vegetables	Colombia	SR-Me	Ap	0.038-0.11	0.025-0.11	PE 2-4

Table 7. Registered uses of haloxyfop on sugar beet. All single applications of EC.

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
Sugar beet	Belarus	R-Me	Ap	0.052-0.1	0.01-0.035	PE 3-5
	Chile	R-Me	Ap	0.045-0.12	0.03-0.12	30
	Chile	SR-Me	Ap	0.09-0.24	0.06-0.24	30
	Croatia	R-Me	Ap	0.052-0.16	0.013-0.078	98
	Czech repub.	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Denmark	SR-EE	Ap	0.1-0.21	0.042-0.21	90
	Ireland	SR-EE	Ap	0.078-0.21	0.02-0.13	GC75%
	Ireland	SR-EE	Ap	0.034	0.034-0.043	GC75%
	France	R-Me	Ap	0.052-0.1	0.13-0.052	ET
	France	SR-EE	Ap	0.1-0.21	0.026-0.1	ET
	Germany	SR-EE	Ap	0.16-0.21	0.039-0.1	90
	Greece	SR-EE	Ap	0.1-0.13	0.026-0.13	90
	Hungary	R-Me	Ap	0.042-0.21	0.014-0.1	100
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Romania	R-Me	Ap	0.1-0.16	0.035-0.078	HC 40
	Russia	R-Me	Ap	0.052-0.1	0.013-0.035	PE 3-5
	Slovakia	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Spain	SR-EE	Ap	0.1-0.42	0.026-0.21	PE 2-4
	The Netherlands	SR-EE	Ap	0.1-0.31	0.026-0.1	ST

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
	Ukraine	R-Me	Ap	0.052-0.1	0.01-0.035	PE 3-5
	Uruguay	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Uruguay	SR-Me	Aer	0.084-0.3	0.17-2.0	PE 2-4
	Uzbekistan	R-Me	Ap	0.1-0.21	0.021-0.069	PE 3-5

Table 8. Registered uses of haloxyfop on legumes except soya beans. All single applications of EC.

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
Beans	Bolivia	SR-Me	Ap	0.06-0.084	0.04-0.084	PE 2-4
	Bolivia	SR-Me	Aer	0.06-0.084	0.12-0.56	E 2-4
	Nicaragua	SR-Me	Ap	0.18-0.24	0.072-0.12	PE 2-4
	South Africa	SR-EE	Ap	0.1-0.31	0.035-0.16	PE 4-6
Broad beans	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	60
Chickpeas	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	98
	Australia	R-Me	Aer	0.04-0.052	>0.13	98
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	98
	Australia	SR-EE	Aer	0.052-0.1	>0.17	98
Faba beans	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	147
	Australia	R-Me	Aer	0.04-0.052	>0.13	147
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	147
	Australia	SR-EE	Aer	0.052-0.1	>0.17	147
Field peas	Australia	R-Me	Ap	0.04-0.078	0.027-0.16	91
	Australia	R-Me	Aer	0.04-0.078	>0.13	91
	Australia	SR-EE	Ap	0.052-0.16	0.035-0.31	91
	Australia	SR-EE	Aer	0.052-0.16	>0.17	91
Legumes	Spain	SR-EE	Ap	0.1-0.21	0.026-0.1	PE 2-4
Lentils	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	119
	Australia	R-Me	Aer	0.04-0.052	>0.13	119
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	119
	Australia	SR-EE	Aer	0.052-0.1	>0.17	119
	Spain	SR-EE	Ap	0.1-0.21	0.026-0.1	PE 2-4
Lupins	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	119
	Australia	R-Me	Aer	0.04-0.052	>0.13	119
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	119
	Australia	SR-EE	Aer	0.052-0.1	>0.17	119
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	60
Navy beans	Australia	R-Me	Ap	0.04-0.078	0.027-0.16	91
	Australia	R-Me	Aer	0.04-0.078	>0.13	91
	Australia	SR-EE	Ap	0.052-0.16	0.035-0.31	91
	Australia	SR-EE	Aer	0.052-0.16	>0.17	91
Peas	Czech repub.	R-Me	Ap	0.052-0.16	0.013-0.078	CC

Crop	Country	Application				PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	60
	Slovakia	R-Me	Ap	0.052-0.16	0.013-0.078	CC

Table 9. Registered uses of haloxyfop on soya beans. All single applications.

Country	Formulation		Application			PHI, days, or growth stage
	Type	ai	Method	kg ai/ha	kg ai/hl	
Argentina	EC	R-Me	Ap	0.042-0.15	0.028-0.15	PE 2-4
Argentina	EC	R-Me	Aer	0.042-0.15	0.084-1.0	PE 2-4
Argentina	EC	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
Argentina	EC	SR-Me	Aer	0.084-0.3	0.17-2	PE 2-4
Australia	EC	R-Me	Ap	0.052-0.078	0.035-0.16	119
Australia	EC	R-Me	Aer	0.052-0.078	>0.17	119
Australia	EC	SR-EE	Ap	0.1-0.16	0.069-0.31	119
Australia	EC	SR-EE	Aer	0.1-0.16	>0.35	119
Bolivia	EC	SR-Me	Ap	0.06-0.084	0.04-0.084	PE 2-4
Bolivia	EC	SR-Me	Aer	0.06-0.084	0.12-0.56	PE 2-4
Brazil	EC	R-Me	Ap	0.096-0.12	0.024-0.06	98
Colombia	EC	R-Me	Ap	0.02-0.08	0.013-0.08	PE 2-4
Colombia	EC	SR-Me	Ap	0.038-0.19	0.025-0.19	PE 2-4
Croatia	EC	R-Me	Ap	0.052-0.16	0.013-0.078	HC 40
Ecuador	EC	SR-Me	Ap	0.06-0.075	0.02-0.038	30
El Salvador	EC	SR-Me	Ap	0.18-0.24	0.072-0.12	PE 2-4
France	EC	R-Me	Ap	0.052-0.1	0.013-0.052	ET
France	EC	SR-EE	Ap	0.052-0.1	0.13-0.052	ET
Guatemala	EC	SR-Me	Ap	0.18-0.24	0.072-0.12	PE 2-4
Honduras	EC	SR-Me	Ap	0.18-0.2	0.072-0.1	PE 2-4
Hungary	EC	R-Me	Ap	0.042-0.21	0.014-0.1	120
Paraguay	LPU	R-Me	Aer	0.045-0.11	0.09-0.7	PE 2-4
Paraguay	EC	SR-Me	Ap	0.072-0.18	0.048-0.18	PE 2-4
Paraguay	EC	SR-Me	Aer	0.072-0.18	0.14-1.2	PE 2-4
Romania	EC	R-Me	Ap	0.1-0.16	0.035-0.078	HC 40
Uruguay	EC	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
Uruguay	EC	SR-Me	Aer	0.084-0.3	0.17-2.0	PE 2-4

Table 10. Registered uses of haloxyfop on rice. All single applications of EC.

Country	Application				PHI, days, or growth stage
	ai	Method	kg ai/ha	kg ai/hl	
Argentina	SR-Me	Ap	0.075-0.09	0.05-0.09	PE 3
Argentina	SR-Me	Aer	0.075-0.09	0.15-0.6	PE 3
Colombia	SR-Me	Ap	0.06-0.09	0.02-0.045	PE 2-4
Colombia	SR-Me	Aer	0.06-0.09	0.12-0.6	PE 2-4
Ecuador	SR-Me	Ap	0.075-0.11	0.025-0.057	PE 2-4
Uruguay	SR-Me	Ap	0.026-0.038	0.017-0.038	PE 2-4
Uruguay	SR-Me	Aer	0.026-0.038	0.052-0.25	PE 2-4

Table 11. Registered uses of haloxyfop on oil seeds and hops. All single applications of EC.

Crop	Country	Formulation, ai	Application			PHI, days, or growth stage
			Method	kg ai/ha	kg ai/hl	
Cotton	Australia	R-Me	Ap	0.052-0.078	0.035-0.16	119
	Australia	R-Me	Aer	0.052-0.078	>0.17	119
	Australia	SR-EE	Ap	0.1-0.16	0.069-0.31	119
	Australia	SR-EE	Aer	0.1-0.16	>0.35	119
	Bolivia	SR-Me	Ap	0.06-0.084	0.04-0.084	PE 2-4
	Bolivia	SR-Me	Aer	0.06-0.084	0.12-0.56	PE 2-4
	Colombia	R-Me	Ap	0.02-0.08	0.013-0.08	PE 2-4
	Colombia	SR-Me	Ap	0.038-0.11	0.025-0.11	PE 2-4
	Ecuador	SR-Me	Ap	0.045-0.06	0.018-0.03	PE 2-4
	El Salvador	SR-Me	Ap	0.12-0.18	0.048-0.09	PE 2-4
	Guatemala	SR-Me	Ap	0.12-0.3	0.048-0.15	PE 2-4
	Honduras	SR-Me	Ap	0.12-0.3	0.048-0.15	PE 2-4
	Paraguay	SR-Me	Ap	0.072-0.18	0.048-0.18	PE 2-4
	Paraguay	SR-Me	Aer	0.072-0.18	0.14-1.2	PE 2-4
	Peru	SR-Me	Ap	0.11-0.15	0.028-0.038	PE 2-4
	Russia	R-Me	Ap	0.052-0.1	0.013-0.035	PE 3-5
	Spain	SR-EE	Ap	0.1-0.42	0.026-0.21	PE 2-4
Palm, African	Costa Rica	SR-Me	Gr	0.29-0.38	0.072-0.096	BF
Palm, oil	Ecuador	SR-Me	Gr	0.06-0.09	0.024-0.045	PE 2-4
Peanuts	Argentina	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Argentina	SR-Me	Aer	0.084-0.3	0.17-2	PE 2-4
	Australia	R-Me	Ap	0.052-0.078	0.035-0.16	119
	Australia	R-Me	Aer	0.052-0.078	>0.17	119
	Australia	SR-EE	Ap	0.1-0.16	0.069-0.31	119
	Australia	SR-EE	Aer	0.1-0.16	>0.35	119
Rape seed	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	119
	Australia	R-Me	Aer	0.04-0.052	>0.13	119

Crop	Country	Formulation, ai	Application			PHI, days, or growth stage
			Method	kg ai/ha	kg ai/hl	
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	119
	Australia	SR-EE	Aer	0.052-0.1	>0.17	119
	Chile	R-Me	Ap	0.03-0.06	0.02-0.06	30
	Chile	SR-Me	Ap	0.06-0.12	0.04-0.12	30
	Croatia	R-Me	Ap	0.052-0.16	0.013-0.078	HC 40
	Czech repub.	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Denmark	SR-EE	Ap	0.1-0.21	0.042-0.21	210
	Ireland	SR-EE	Ap	0.078-0.21	0.02-0.1	end of Dec.
	France	R-Me	Ap	0.052-0.1	0.13-0.052	ET
	France	SR-EE	Ap	0.1-0.21	0.026-0.1	ET
	Germany	SR-EE	Ap	0.1-0.21	0.026-0.052	PE
	Hungary	R-Me	Ap	0.042-0.21	0.014-0.1	80
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Slovakia	R-Me	Ap	0.052-0.13	0.013-0.065	CC
	Spain	SR-EE	Ap	0.1-0.42	0.026-0.21	PE 2-4
	The Netherlands	SR-EE	Ap	0.1-0.31	0.026-0.1	ST
Sunflower	Argentina	R-Me	Ap	0.042-0.15	0.028-0.15	PE 2-4
	Argentina	R-Me	Aer	0.042-0.15	0.084-1.0	PE 2-4
	Argentina	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Argentina	SR-Me	Aer	0.084-0.3	0.17-2	PE 2-4
	Australia	R-Me	Ap	0.052-0.078	0.035-0.16	119
	Australia	R-Me	Aer	0.052-0.078	>0.17	119
	Australia	SR-EE	Ap	0.1-0.16	0.069-0.31	119
	Australia	SR-EE	Aer	0.1-0.16	>0.35	119
	Bolivia	SR-Me	Ap	0.06-0.084	0.04-0.084	PE 2-4
	Bolivia	SR-Me	Aer	0.06-0.084	0.12-0.56	PE 2-4
	Chile	R-Me	Ap	0.045-0.12	0.03-0.12	30
	Chile	SR-Me	Ap	0.09-0.24	0.06-0.24	30
	Croatia	R-Me	Ap	0.052-0.16	0.013-0.078	98
	Czech repub.	R-Me	Ap	0.052-0.16	0.013-0.078	CC
	France	R-Me	Ap	0.052-0.1	0.13-0.052	ET
	France	SR-EE	Ap	0.1-0.21	0.026-0.1	ET
	Greece	SR-EE	Ap	0.1-0.13	0.026-0.13	PE
	Hungary	R-Me	Ap	0.042-0.21	0.014-0.1	90
	Paraguay	SR-Me	Ap	0.072-0.18	0.048-0.18	PE 2-4
	Paraguay	SR-Me	Aer	0.072-0.18	0.14-1.2	PE 2-4
	Romania	R-Me	Ap	0.1-0.16	0.035-0.078	HC 40
	Slovakia	R-Me	Ap	0.052-0.16	0.013-0.078	CC
	Uruguay	SR-Me	Ap	0.084-0.3	0.056-0.3	PE 2-4
	Uruguay	SR-Me	Aer	0.084-0.3	0.17-2.0	PE 2-4
Hops	Czech repub.	R-Me	Gr	0.052-0.13	0.013-0.065	CC
	Slovakia	R-Me	Gr	0.052-0.13	0.013-0.065	CC

Table 12. Registered uses of haloxyfop on animal feed crops. All EC formulations.

Crop	Country	Application					PHI, days, or growth stage
		ai	Method	kg ai/ha	kg ai/hl	No.	
Alfalfa	Australia	R-Me	Ap	0.04-0.078	0.027-0.16	1	21
	Australia	R-Me	Aer	0.04-0.078	>0.13	1	21
	Australia	SR-EE	Ap	0.052-0.16	0.035-0.31	1	21
	Australia	SR-EE	Aer	0.052-0.16	>0.17	1	21
	Czech repub.	R-Me	Ap	0.052-0.16	0.013-0.078	1	CC
	Peru	SR-Me	Ap	0.11-0.15	0.028-0.038	1	PE 2-4
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	1	CC
	Slovakia	R-Me	Ap	0.052-0.16	0.013-0.078	1	CC
Fodder beet	Belarus	R-Me	Ap	0.052-0.1	0.01-0.035	1	PE 3-5
	Ireland	SR-EE	Ap	0.078-0.21	0.02-0.13	1	GC75%
	Ireland	SR-EE	Ap	0.034	0.034-0.043	3	GC75%
	France	SR-EE	Ap	0.1-0.21	0.026-0.1	1	ET
	Germany	SR-EE	Ap	0.16-0.21	0.039-0.1	1	90
	Poland	R-Me	Ap	0.052-0.13	0.013-0.065	1	60
	Russia	R-Me	Ap	0.052-0.1	0.013-0.035	1	PE 3-5
	The Netherlands	SR-EE	Ap	0.1-0.31	0.026-0.1	1	ST
	Ukraine	R-Me	Ap	0.052-0.1	0.01-0.035	1	PE 3-5
	Uzbekistan	R-Me	Ap	0.1-0.21	0.021-0.069	1	PE 3-5
Fodder peas (spring)	France	R-Me	Ap	0.052-0.1	0.13-0.052	1	ET
Fodder peas (winter)	France	R-Me	Ap	0.052-0.1	0.13-0.052	1	ET
Forage legumes	Uruguay	SR-Me	Ap	0.084-0.3	0.056-0.3	1	PE 2-4
	Uruguay	SR-Me	Aer	0.084-0.3	0.17-2.0	1	PE 2-4
Pasture	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	1	7
	Australia	R-Me	Aer	0.04-0.052	>0.13	1	7
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	1	7
	Australia	SR-EE	Aer	0.052-0.1	>0.17	1	7
Vetch	Australia	R-Me	Ap	0.04-0.052	0.027-0.104	1	91
	Australia	R-Me	Aer	0.04-0.052	>0.13	1	91
	Australia	SR-EE	Ap	0.052-0.1	0.035-0.21	1	91
	Australia	SR-EE	Aer	0.052-0.1	>0.17	1	91

RESIDUES RESULTING FROM SUPERVISED TRIALS

Supervised trials were carried out on fruits, vegetables, legume crops, oil seed, rice and animal feed crops with ethoxyethyl, butyl or methyl esters of haloxyfop.

Underlined residues in the Tables are from treatments according to GAP.

Application rates are expressed as free haloxyfop acid equivalents and residues have not normally been corrected for recoveries.

The following abbreviations are used in the Tables.

Active ingredient

SR:	racemic haloxyfop
R:	resolved (*R*)- isomer of haloxyfop
Me:	methyl ester
EE:	ethoxyethyl ester
Bt:	butyl ester

Residues in crops

Fruits

Citrus fruit. Eight supervised trials were carried out on oranges, lemons and grapefruit in Brazil, Italy and New Zealand with 0.16-1.9 kg ai/ha of racemic haloxyfop and haloxyfop-R. All residues were below the LODs of 0.01-0.1 mg/kg at PHIs of 28-206 days (Table 13).

Table 13. Residues of haloxyfop in citrus fruits. All single applications.

Crop, Country, Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound Form.	kg ai/ha	kg ai/hl				
Oranges	SR-Me	0.24	N.S.[1]	67	N.S.	<0.1	GHB-P040
Brazil	EC	0.48	N.S.	67		<0.1	(N136)
1986		0.72	N.S.	67		<0.1	
		0.96	N.S.	67		<0.1	
		1.4	N.S.	67		<0.1	
		1.9	N.S.	67		<0.1	
Oranges	SR-Me	0.24	0.08	206	N.S.	<0.1	GHB-P040
Brazil	EC	0.48	0.16	206		<0.1	(N136)
1986		0.72	0.24	206		<0.1	
		0.96	0.32	206		<0.1	
		1.4	0.48	206		<0.1	
		1.9	0.64	206		<0.1	
Oranges	R-Me	0.16	0.031	56	fruit diameter 6.5 cm	<0.02[2]	GHE-P-2771
Italy, 1991	EC			56		<0.02[3]	(N140)
Oranges	R-Me	0.16	0.031	56	fruit diameter 5.5 cm	<0.02[2]	GHE-P-2771
Italy, 1991	EC			56		<0.02[3]	(N140)
Lemons	SR-EE	0.42	0.042	28	beginning to	<0.03	GHF-P1147
New Zealand, 1991	EC	0.83	0.083	28	ripen	<0.03	(N135)
Lemons	R-Me	0.21	0.021	28	beginning to	<0.03	GHF-P1147
New Zealand, 1991	EC	0.42	0.042	28	ripen	<0.03	(N135)
Lemons	R-Me	0.21	0.021	28	beginning to	<0.03	GHF-P1147
New Zealand, 1991	WDG[4]	0.42	0.042	28	ripen	<0.03	(N135)
Grapefruit	SR-EE	0.21	0.1	29	N.S.	<0.01	GHF-P-515
New Zealand, 1985	EC	0.42	0.21	29		<0.01	(N137)

[1] Not specified in report
[2] Peel
[3] Pulp
[4] Water dispersible granule

Apples. Three supervised trials were carried out in Italy and New Zealand with single applications of haloxyfop-etotyl EC at 0.1- 0.42 kg ai/ha. Residues were <0.01 or <0.02 mg/kg at all application rates with PHIs of 29-132 days (Table 14).

Table 14. Residues of haloxyfop in apples.

Country, year	Application		PHI, days	Growth at last treatment	Residues, mg/kg	Reference
	kg ai/ha	kg ai/hl				
Italy 1987	0.1	N.S.[1]	132	fruit setting	<0.02	GHE-P-1965 (N96)
	0.21	N.S.	132		<0.02	
	0.42	N.S.	132		<0.02	
Italy 1987	0.1	N.S.	126	fruit setting	<0.02	GHE-P-1965 (N96)
	0.21	N.S.	126		<0.02	
	0.42	N.S.	126		<0.02	
New Zealand 1986	0.21	0.1	29	N.S.	<0.01	GHF-P-584 (N97)
	0.42	0.21	29		<0.01	

[1] Not specified in report

Grapes. Six supervised trials were carried out in Australia and France with 0.21-1.7 kg ai/ha of racemic haloxyfop-etotyl. Residues were below or near the LOD of 0.01 or 0.03 mg/kg at PHIs of 21-119 days. In three supervised trials in Italy with 0.21 kg ai/ha of haloxyfop-R-methyl residues were <0.05 mg/kg (Table 15).

Table 15. Residues of haloxyfop in grapes. All EC formulations.

Country Year	Application[1]				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No	kg ai/ha	kg ai/hl				
Australia	SR-EE	1	0.21	0.21	21	21:bunches	<0.03	GHF-P-1150
1990					49	almost full	<0.03	(N102A)
		1	0.42	0.42	21		<0.03	
					49	49:bunches	<0.03	
		1	0.83	0.83	21	half filled	<0.03	
					49		<0.03	
Australia	SR-EE	1	0.21	0.21	29	29:bunches	<0.03	GHF-P-1150
1990					56	almost full	<0.03	(N102A)
		1	0.42	0.42	29		<0.03	
					56	56: start of	<0.03	
		1	0.83	0.83	29	bunching	0.03	
					56		<0.03	
France	SR-EE	2	0.1	0.016	93		<0.01	GHE-P-1148
1983		2	0.21	0.032	93	N.S.	<0.01	(N101)
		2	0.42	0.064	93		<0.01	
		2	0.83	0.13	93		<0.01	
		2	1.7	0.26	93		<0.01	
France 1985	SR-EE	1	0.42	N.S.	119	N.S.	<0.01	GHE-P-1532
		1	0.83	N.S.	119		<0.01	(N102)
France 1985	SR-EE	1	0.42	0.1	115	N.S.	<0.01	GHE-P-1532
		1	0.83	0.21	115		<0.01	(N102)
France 1985	SR-EE	1	0.42	0.14	86	N.S.	<0.01	GHE-P-1532
		1	0.83	0.28	86		<0.01	(N102)
Italy 1989	R-Me	1	0.21	0.052	67	small pea size	<0.05	GHE-P-2115 (N70)
Italy 1989	R-Me	1	0.21	0.052	63	small pea size	<0.05	GHE-P-2115 (N70)
Italy 1989	R-Me	1	0.21	0.052	51	small pea size	<0.05	GHE-P-2115 (N70)

[1] Not specified in report

Bananas. Two supervised trials were carried out in Australia, one with 0.83 kg ai/ha of racemic haloxyfop-etotyl and the other with 0.42 kg ai/ha of haloxyfop-R-methyl. Residues were <0.05 mg/kg at PHIs of 7-14 days (Table 16).

Table 16. Residues of haloxyfop in bananas in Australia, 1991. All single applications.

Compound, form.	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	kg ai/ha	kg ai/hl				
SR-EE	0.83	0.5	14	bunching	<0.05	GHF-P-1149
EC						(N133)
R-Me	0.42	0.25	7	bunching	<0.05	GHF-P-1149
WDG			14		<0.05	

Vegetables (Table 17)

Garlic. Two supervised trials were carried out in Spain at application rates of 0.078 or 0.16 kg ai/ha of haloxyfop-R-methyl with PHIs of 53 and 88 days.

Onions. Four supervised trials were carried out in Greece, The Netherlands, New Zealand and the UK at application rates of 0.052-0.83 kg ai/ha with PHIs of 15-121 days.

Cabbage. Two supervised trials were carried out in the UK and New Zealand at application rates of 0.052-0.42 kg ai/ha with PHIs of 14-65 days.

Brussels sprouts. Two supervised trials in the UK were with haloxyfop-etotyl at 0.21 and 0.42 kg ai/ha, both with a PHI of 147 days.

Cauliflower. Two UK trials were at application rates of 0.21 and 0.42 kg ai/ha with PHIs of 48 days.

Melons. Two supervised trials were carried out in Italy at an application rate of 0.052 kg ai/ha with haloxyfop-R-methyl with PHIs of 46 and 60 days.

Tomatoes. Four trials were carried out in Australia with racemic haloxyfop-etotyl at application rates of 0.1 and 0.2 kg/ha, and 6 in Italy with 0.052 and 0.1 kg ai/ha of haloxyfop-R-methyl. PHIs were 41-74 days.

Fennel. Only one supervised trial was reported to the Meeting, which was in Italy with haloxyfop-R-methyl at an application rate of 0.062 kg ai/ha. Samples were taken at 72 and 165 days.

Lettuce. Two supervised trials were carried out in Spain at application rates of 0.052-0.16 kg ai/ha with haloxyfop-R-methyl, with PHIs of 40 and 50 days.

Spinach. Two trials were carried out in Italy at an application rate of 0.062 kg ai/ha with haloxyfop-R-methyl. The PHIs were 28 and 32 days.

Carrots. Three supervised trials in Italy were with haloxyfop-R-methyl at an application rate of 0.052 kg ai/ha and PHIs of 38-138 days.

Artichokes. Two trials with haloxyfop-R-methyl in Spain were at application rates of 0.052 and 0.078 kg ai/ha with PHIs of 0-42 days.

Asparagus. Two supervised trials in Italy were at an application rate of 0.062 kg ai/ha with haloxyfop-R-methyl with PHIs of 21 and 28 days.

Table 17. Residues of haloxyfop in vegetables. All single applications of EC.

Crop, Country, Year	Compound	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
		kg ai/ha	kg ai/hl				
Garlic	R-Me	0.078	0.022	88	6-7 leaves	<0.02	GHE-P-2066
Spain 1989		0.16	0.045	88	20 cm height	<0.02	(N40)
Garlic	R-Me	0.078	0.022	53	7-8 leaves	<0.02	GHE-P-2066
Spain 1989		0.16	0.045	53	40 cm height	0.02	(N40)
Onions	SR-EE	0.1	N.S.[1]	33		<0.02	GHE-P-1497
Greece		0.21	N.S.	33	25-30 cm	0.04	(N88)
1985		0.42	N.S.	33	height	0.05	
		0.83	N.S.	33		0.11	
Onions	SR-EE	0.21	N.S.	121		<0.02	GHE-P-1498
Netherlands		0.31	N.S.	121	20 cm height	<0.02	(N87)
1984		0.42	N.S.	121		<0.02	
Onions	SR-EE	0.1	0.052	80	2-3 leaves	<0.02	GHE-P-1499
UK		0.21	0.1	80	10-15 cm	<0.02	(N86)
1985		0.42	0.21	80	height	0.03	
Onions	SR-EE	0.052	0.026	15	15:mature	<0.005	GHF-P-633
New Zealand				30	bulbs,tops	0.008	(N89)
1987		0.1	0.052	15	beginning to	0.013	
				30	collapse	0.023	
		0.21	0.1	15	30: mature	0.029	
				30	bulbs, green leaves	0.058	
Cabbage	SR-EE	0.21	N.S.	65	4 expanded	<0.02(H)[2]	GHE-P-2738
UK				65	true leaves	<0.02(O)[3]	(N91A)
1991		0.42	N.S.	65		<0.02(H)	
				65		<0.02(O)	
Cabbage	SR-EE	0.052	0.026	14		0.113	GHF-P-632
New Zealand				29	N.S.	0.132	(N91)
1987		0.1	0.052	14		0.131	
				29		0.168	
		0.21	0.1	14		0.311	
				29		0.231	
Brussels	SR-EE	0.21	0.1	147		0.06(B)[4]	GHE-P-2738
sprouts				147	stem	0.07(T)[5]	(N91A)
UK		0.42	0.21	147	extension	0.16(B)	
1991				147		0.1(T)	
Cauliflower	SR-EE	0.21	0.1	48		0.29(C)[6]	GHE-P-2738
UK				48	button	0.18(O)	(N91A)
1991		0.42	0.21	48	formation	0.48(C)	
				48		0.41(O)	
Melon Italy 1990	R-Me	0.052	N.S.	60	flowering	<0.02	GHE-P2410 (N110)
Melon Italy 1990	R-Me	0.052	N.S.	46	flowering	<0.02	GHE-P-2410 (N110)
Tomato	SR-EE	0.1	N.S.	74	15 cm height	<0.02	PAU-3312-156
Australia 1984		0.2	N.S.	74	first flower formed	0.02	(N117)
Tomatoes	R-Me	0.052	0.013	41	fruit setting	0.03	GHE-P-2116

Crop, Country, Year	Compound	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
		kg ai/ha	kg ai/hl				
Italy 1989		0.1	0.026	41		0.07	(N60)
Tomatoes	R-Me	0.052	0.013	52	fruit setting	<0.02	GHE-P-2116
Italy 1989		0.1	0.026	52		<0.02	(N60)
Tomatoes	R-Me	0.052	0.013	52	fruit setting	0.02	GHE-P-2116
Italy 1989		0.1	0.026	52		0.03	(N60)
Fennel	R-Me	0.062	0.016	72	4 leaves	<0.02	GHE-P-2796
Italy 1992				165	2 leaves	<0.02	(N45)
Lettuce	R-Me	0.052	N.S.	40		0.06	GHE-P-2184
Spain		0.1	N.S.	40	13 leaves	0.07	(N90)
1990		0.16	N.S.	40		0.14	
Lettuce	R-Me	0.052	N.S.	50		0.08	GHE-P-2184
Spain		0.1	N.S.	50	15-16 leaves	0.1	(N90)
1990		0.16	N.S.	50		0.13	
Spinach Italy 1992	R-Me	0.062	0.016	28	2 leaves	0.05	GHE-P-3038 (N95)
Spinach Italy 1992	R-Me	0.062	0.016	32	3 leaves	0.04	GHE-P-3038 (N95)
Carrots Italy 1991	R-Me	0.052	N.S.	65	4 leaves	<0.02	GHE-P-2539 (N130)
Carrots Italy 1991	R-Me	0.052	N.S.	138	6 leaves	<0.02	GHE-P-2539 (N130)
Carrots Italy 1991	R-Me	0.052	N.S.	38	6 leaves	<0.02	GHE-P-2539 (N130)
Artichoke	R-Me	0.052	N.S.	0		0.06	GHE-P-2185
Spain				7	all leaves	0.07	(N100)
1990				14	open-full	0.1	
				30	florescence	0.1	
				42		0.05	
		0.078	N.S.	0		0.09	
				7		0.1	
				14		0.15	
				30		0.14	
				42		0.04	
Artichokes	R-Me	0.052	N.S.	0		0.07	GHE-P-2185
Spain				7	all leaves	0.06	(N100)
1990				14	open-full	0.08	
				30	florescence	0.06	
				42		0.03	
		0.078	N.S.	0		0.13	
				7		0.12	
				14		0.15	
				30		0.11	
				42		0.08	
Asparagus Italy 1992	R-Me	0.062	0.016	21	3 cm length	<0.02	GHE-P-2800
Asparagus Italy 1992	R-Me	0.062	0.016	28	4 cm length	<0.02	GHE-P-2800

[1] Not specified
[2] Heart
[3] Outer leaves
[4] Buttons

[5] Plant tops
[6] Curd

Peas (pods and succulent seeds). Four supervised trials in France with racemic haloxyfop-etotyl were at 0.1 or 0.21 kg ai/ha with PHIs of 36-68 days. Three others in France and four in Germany were with haloxyfop-R-methyl at 0.052 or 0.1 kg ai/ha with PHIs of 36-60 days (Table 18).

Table 18. Residues of haloxyfop in peas. All single EC applications.

Country, year	Application			PHI, days	Growth stage at last treatment[1]	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
France 1984	SR-EE	0.1	0.016	68	15-20 cm height	0.07	GHE-P-1671 (N66)
France 1988	SR-EE	0.1	N.S.[1]	39	8-9 leaves	<0.05	GHE-P-1956
		0.21	N.S.	39		0.11	(N30)
France 1989	SR-EE	0.1	0.021	36	5-6 leaves	0.03	GHE-P-2057
		0.21	0.042	36		0.06	(N31)
France 1989	SR-EE	0.1	0.042	36	flower buds	0.04	GHE-P-2057
		0.21	0.084	36	hidden by top leaves	0.07	(N31)
France 1988	R-Me	0.052	N.S.	39	8-9 leaves	<0.05	GHE-P-1956
		0.1	N.S.	39		0.06	(N30)
France 1989	R-Me	0.052	0.01	36	5-6 leaves	0.03	GHE-P-2057
		0.1	0.021	36		0.04	(N31)
France 1989	R-Me	0.052	0.021	36	flower buds hidden by top leaves	0.03	GHE-P-2057
		0.1	0.042	36		0.05	(N31)
Germany 189	R-Me	0.1	0.035	43	3 leaves	<0.02[2]	GHE-P-2154
				56		<0.02	(N36)
Germany 1989	R-Me	0.1	0.035	38	4 leaves	<0.02[2]	GHE-P-2154
				53		<0.02	(N36)
Germany 1989	R-Me	0.1	0.026	42	10 leaves	0.07[2]	GHE-P-2154 (N36)
Germany 1989	R-Me	0.1	0.026	42	6-7 leaves	0.03[2]	GHE-P-2154
				60		<0.02	(N36)

[1] Not specified [2] Pod

Field beans. Eight supervised trials were conducted in Germany with haloxyfop-R-methyl at application rates of 0.052 or 0.1 kg ai/ha with PHIs of 42-80 days (Table 19).

Table 19. Residues of haloxyfop in field beans in Germany. All single EC applications of haloxyfop-R-methyl.

Year	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	kg ai/ha	kg ai/hl				
1989	0.1	0.035	55	4 leaves	0.02[1]	GHE-P-2155 (N35)

Year	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	kg ai/ha	kg ai/hl				
1989	0.1	0.035	46	4 leaves	0.03[1]	GHE-P-2155 (N35)
1989	0.1	0.026	71	6 leaves	<0.02[1]	GHE-P-2155 (N35)
1989	0.1	0.026	42	6 leaves	0.03[1]	GHE-P-2155 (N35)
1990	0.052	0.013	76 76	6 leaves	<0.02 <0.02[1]	GHE-P-2444 (N37)
	0.1	0.026	76 76		<0.02 <0.02[1]	
1990	0.052	0.013	70 70	4-5 leaves	<0.02 <0.02[1]	GHE-P-2444 (N37)
	0.1	0.026	70 70		<0.02 <0.02[1]	
1990	0.052	0.013	80 80	4 leaves	<0.02 <0.02[1]	GHE-P-2444 (N37)
	0.1	0.026	80 80		<0.02 <0.02[1]	
1990	0.052	0.013	62 62	beginning of flowering	0.06 <0.02[1]	GHE-P-2444 (N37)
	0.1	0.026	62 62		0.16 0.02[1]	

[1] Pod

Broad beans (dry). Four supervised trials were carried out in Australia, France and Greece with racemic haloxyfop-etotyl at 0.078-0.26 kg ai/ha with PHIs of 16-171 days (Table 20).

Table 20. Residues of haloxyfop in broad beans (dry). All single EC applications of haloxyfop-etotyl.

Country, year	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	kg ai/ha	kg ai/hl				
Australia 1986	0.078	N.S.[1]	171	43 days after planting	<0.05	PAU-3313-269
	0.16	N.S.	171		<0.05	(N63)
Australia 1988	0.1	0.065	103	6-8 leaves 55 days after planting	<0.05	GHF-P-834
	0.21	0.13	103		<0.05	(N65A)
France 1984	0.21	0.032	46	24 days after planting	0.03	GHE-P-1693 (N61)
Greece 1983	0.16	N.S.	16	maturing beans	0.37	GHE-P-1694
	0.26	N.S.	16		0.73	(N62)

[1] Not specified

Chick-peas and pigeon peas (dry). Three supervised trials were carried out in Australia on chick-peas with haloxyfop-etotyl at 0.1-0.42 kg ai/ha and two on pigeon peas with etotyl at 0.16 or 0.31 kg ai/ha and with haloxyfop-R-methyl at 0.038 or 0.075 kg ai/ha. PHIs were 52-137 days (Table 21).

Table 21. Residues of haloxyfop in chick-peas (dry) and pigeon peas (dry) in Australia. All single EC applications.

Crop, year	Application			PHI days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Chick-peas	SR-EE	0.1	0.095	52	52:full	0.3	PAU-3313-254
				65	bloom	0.09	(N70)
1986				79	65:mid to	0.03	
		0.21	0.19	52	late	0.65	
				65	tillering	0.18	
				79	79:3-5	0.05	
		0.42	0.38	79	leaves	0.06	
Chick-peas	SR-EE	0.1	0.095	65	65:full	0.11	PAU-3313-254
				78	bloom	0.04	(N70)
1986				137	78:mid to	<0.03	
		0.21	0.19	65	late	0.16	
				78	tillering	0.05	
				137	137:3-5	<0.03	
		0.42	0.38	137	leaves	<0.03	
Chick-peas	SR-EE	0.1	0.095	65	65:full	0.19	PAU-3313-254
				78	bloom	0.06	(N70)
1986				99	78:mid to	<0.03	
		0.21	0.19	65	late	0.24	
				78	tillering	0.09	
				99	99:3-5	<0.03	
		0.42	0.38	99	leaves	0.06	
Pigeon peas	SR-EE	0.16	0.14	85	43 days	0.03	GHF-P-895
1989		0.31	0.28	85	after planting	0.06	(N70A)
Pigeon peas	R-Me	0.038	0.035	85	43 days	<0.01	GHF-P-895
1989		0.075	0.068	85	after planting	0.02	(N70A)

Common beans (dry). Five supervised trials were carried out in Australia, Brazil and the UK with 0.12-0.48 kg ai/ha of racemic haloxyfop methyl and etotyl esters, with PHIs of 24-104 days.

Nine supervised trials in Germany and the UK at 0.052-0.21 kg ai/ha were with haloxyfop-R-methyl with PHIs, of 72-120 days (Table 22).

Table 22. Residues of haloxyfop in common beans (dry). All single EC applications.

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Australia 1986	SR-EE	0.16	0.14	24	24:mature	0.07	PAU-3313-249
				64	pod	0.05	(N80C)

				75	64:early	0.03	
		0.31	0.3	24	bloom	0.04	
				64	75:6 leaves	0.13	
				75		0.05	
Australia 1989	SR-EE	0.16	0.14	85	early	0.41	GHF-P-919
		0.31	0.28	85	budding	0.87	(N64)
Brazil 1987	SR-Me	0.12	0.052	68		<0.05	GHB-P072
		0.24	0.1	68	2 trifoliate	<0.05	(N145)
		0.48	0.21	68		<0.05	
Brazil 1987	SR-Me	0.12	0.048	76	16 days	<0.05	GHB-P072
		0.24	0.96	76	post	<0.05	(N145)
		0.48	0.19	76	emergence	<0.05	
UK 1991	SR-EE	0.21	N.S.[1]	104	end of	0.2	GHE-P-2654
		0.42	N.S.	104	flowering	0.31	(N65)
Germany 1989	R-Me	0.1	0.035	89	4 leaves	<0.02	GHE-P-2155 (N35)
Germany 1989	R-Me	0.1	0.035	91	4 leaves	0.04	GHE-P-2155 (N35)
Germany 1989	R-Me	0.1	0.026	120	6 leaves	<0.02	GHE-P-2155 (N35)
Germany 1989	R-Me	0.1	0.026	105	6 leaves	0.03	GHE-P-2155 (N35)
Germany 1990	R-Me	0.052	0.013	91	6 leaves	<0.02	GHE-P-2444
		0.1	0.026	91		0.02	(N37)
Germany 1990	R-Me	0.052	0.013	98	4-5 leaves	<0.02	GHE-P-2444
		0.1	0.026	98		<0.02	(N37)
Germany 1990	R-Me	0.052	0.013	106	4 leaves	<0.02	GHE-P-2444
		0.1	0.026	106		<0.02	(N37)
Germany 1990	R-Me	0.052	0.013	72	beginning	0.11	GHE-P-2444
		0.1	0.026	72	of flowering	0.3	(N37)
UK 1991	R-Me	0.1	N.S.	104	end of	0.1	GHE-P-2654
		0.21	N.S.	104	flowering	0.18	(N38)

[1] Not specified

Field peas (dry). Ten supervised trials in Australia and France were with racemic haloxyfop-etotyl at 0.06-0.21 kg ai/ha, and 12 in Australia, France, and Germany were with haloxyfop-R-methyl at 0.052-0.1 kg ai/ha. PHIs were 68-168 days (Table 23).

Table 23. Residues of haloxyfop in field peas (dry). All single EC applications.

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Australia 1984	SR-EE	0.06	0.038	168	6-8 weeks	<0.02	PAU-3313-200
		0.12	0.075	168	after planting	<0.02	(N68)
Australia 1984	SR-EE	0.062	0.12	151	2-3 leaves	<0.01	PAU-3313-211
		0.13	0.25	151		<0.01	(N69)
		0.062	0.12	132	early	<0.01	
		0.13	0.25	132	tillering	<0.01	
Australia 1989	SR-EE	0.1	0.1	94	14 cm	<0.01	GHF-P-1003
		0.21	0.21	94	height	<0.01	(N70C)
Australia 1989	SR-EE	0.1	0.1	93	2-3 nodes,	<0.01	GHF-P-1003
		0.21	0.21	93	6-10 cm height	<0.01	(N70C)
(Winter) France 1989	SR-EE	0.1	0.032	68	5-6 spread	0.04	GHE-P-2058
		0.21	0.064	68	out leaves	0.06	(N32)
(Winter) France 1989	SR-EE	0.1	0.031	99	6-7 spread	<0.02	GHE-P-2058
		0.21	0.062	99	out leaves	<0.02	(N32)
(Winter) France 1989	SR-EE	0.1	0.031	99	6 leaves	<0.02	GHE-P-2058
		0.21	0.062	99		<0.02	(N32)
(Spring) France 1989	SR-EE	0.1	0.026	80	6 spread out	<0.02	GHE-P-2055
		0.21	0.052	80	leaves	<0.02	(N33)
(Spring) France 1988	SR-EE	0.1	0.035	92		0.07	GHE-P-1966
		0.21	0.07	92	9-10 leaves	0.14	(N34)
(Spring) France 1988	SR-EE	0.1	N.S.[1]	109	4 leaves	<0.05	GHE-P-1966
		0.21	N.S.	109		<0.05	(N34)
Australia 1989	R-Me	0.052	0.052	94	14 cm height	<0.01	GHF-P-1003
		0.1	0.1	94		<0.01	(N70C)
Australia 1989	R-Me	0.052	0.052	93	2-3 nodes,	<0.01	GHF-P-1003
		0.1	0.1	93	6-10 cm height	<0.01	(N70C)
(Winter) France 1989	R-Me	0.052	0.016	68	5-6 spread	0.04	GHE-P-2058
		0.1	0.032	68	out leaves	0.06	(N32)
(Winter) France 1989	R-Me	0.052	0.016	99	6-7 spread	<0.02	GHE-P-2058
		0.1	0.032	99	out leaves	<0.02	(N32)
(Winter) France 1989	R-Me	0.052	0.016	99	6 leaves	<0.02	GHE-P-2058
		0.1	0.032	99		<0.02	(N32)
(Spring)	R-Me	0.052	0.013	80	6 spread	<0.02	GHE-P-2055

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
France 1989		0.1	0.026	80	out leaves	<0.02	(N33)
(Spring) France 1988	R-Me	0.052	0.017	92	9-10 leaves	<0.05	GHE-P-1966
		0.1	0.035	92		0.1	(N34)
(Spring) France 1988	R-Me	0.052	N.S.	109	4 leaves	<0.05	GHE-P-1966
		0.1	N.S.	109		<0.05	(N34)
Germany 1989	R-Me	0.1	0.035	76	3 leaves	<0.02	GHE-P-2154 (N36)
Germany 1989	R-Me	0.1	0.035	77	4 leaves	<0.02	GHE-P-2154 (N36)
Germany 1989	R-Me	0.1	0.026	60	10 leaves	0.03	GHE-P-2154 (N36)
Germany 1989	R-Me	0.1	0.026	80	6-7 leaves	0.03	GHE-P-2154 (N36)

[1] Not specified

Lupins (dry). Ten supervised trials were carried out in Australia, 18 with racemic haloxyfop-etotyl at 0.06-0.24 kg ai/ha and one with haloxyfop-R-methyl at 0.052-0.1 kg ai/ha, with PHIs of 92-192 days (Table 24).

Table 24. Residues of haloxyfop in lupins (dry) in Australia. All single EC applications.

Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
1984	SR-EE	0.06	0.067	157	2-3 pairs	0.05	PAU-3313-202
				172	of leaves	0.04	(N81)
1984	SR-EE	0.06	0.067	154	2-3 pairs	0.03	PAU-3313-202
				169	of leaves	0.03	(N81)
1984	SR-EE	0.06	N.S.[1]	127	3-4 pairs	<0.02	PAU-3313-203
				141	of leaves	<0.02	(N82)
1984	SR-EE	0.06	N.S.	156	2-3 nodes	<0.02	PAU-3313-203
		0.12	N.S.	156		<0.02	(N82)
1984	SR-EE	0.24	0.12	167	8 leaves	<0.02	PAU-3313-203 (N82)
1986	SR-EE	0.078	0.078	99	N.S.	<0.05	PAU-3313-264
				139	N.S.	<0.05	(N83)
				154	12 cm height	<0.05	
				181	2-3	<0.05	
		0.16	0.16	99	leaves	0.04	
				139		<0.05	
				154		<0.05	
1986	SR-EE	0.078	0.078	179	4-6 leaves	<0.05	PAU-3313-264
		0.21	0.21	179	10 cm height	<0.05	(N83)

haloxyfop

Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
1986	SR-EE	0.078	0.078	115	11-12 leaves	<0.05	PAU-3313-264
		0.16	0.16	115	15 cm height	<0.05	(N83)
		0.1	0.1	135		<0.05	
		0.21	0.21	135		<0.05	
1985	SR-EE	0.06	0.079	110	8 leaves	<0.03	PAU-3313-250
		0.12	0.16	110		0.03	(N85A)
		0.24	0.32	110		0.03	
1989	SR-EE	0.1	0.1	92	50 cm	0.11	GHF-P-1004
				154	height, just	0.01	(N84)
				192	before	<0.01	
		0.21	0.21	92	flowering	0.2	
				154		0.01	
				192		<0.01	
1989	R-Me	0.052	0.052	92		0.05	GHF-P-1004
				154	10-15 cm height	<0.01	(N84)
				192		<0.01	
		0.1	0.1	92		0.116	
				154		<0.01	
				192	6 leaves 7-10 cm height	<0.01	

[1] Not specified

Soya beans (dry). Thirty three supervised trials were carried out in Australia, Brazil and the USA with the methyl, butyl and ethoxyethyl esters of racemic haloxyfop at 0.06-0.48 kg ai/ha with PHIs of 55-142 days. In 20 trials in France and Italy haloxyfop-R-methyl was applied at 0.052-0.1 kg ai/ha. PHIs were 76-133 days (Table 25).

Table 25. Residues of haloxyfop in soya beans (dry).

Country, Year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound, Form.	No	kg ai/ha	kg ai/hl				
Australia 1986	SR-EE	1	0.16	0.16	55	bloom/early pod	0.16	PAU-3313-249
	EC				102	pre-bloom	<0.03	(N80C)
		1	0.31	0.31	55		0.03	
					102		0.03	
Australia 1986	SR-EE	1	0.16	0.17	105	4 leaves	<0.03	PAU-3313-249
	EC							(N80C)
Australia 1986	SR-EE	1	0.16	0.14	110	4 leaves	<0.03	PAU-3313-249
	EC				122	1-2 leaves	<0.03	(N80C)
		1	0.31	0.29	110		<0.03	
					122		<0.03	
Australia 1986	SR-EE	1	0.21	0.19	94	3 leaves	<0.03	PAU-3313-249
	EC	1	0.31	0.29	94		0.03	(N80C)
		1	0.42	0.38	94		0.03	
		2	0.12	0.095	43	early to pod	.33	
		2	0.16	0.14	43		0.43	
		2	0.2	0.19	43		0.46	
Brazil 1984	SR-Me	1	0.12	0.05	105	pre-bloom,	<0.05	GHB-P024
	EC	1	0.24	0.1	105	3rd trifoliate	<0.05	(N79)
		1	0.36	0.14	105		0.13	
Brazil 1984	SR-Me	1	0.12	0.05	60	in bloom	1.02	GHB-P024
	EC	1	0.24	0.1	60		0.8	(N79)
		1	0.36	0.14	60		1.46	
Brazil 1984	SR-Me	1	0.12	0.04	99	pre-bloom,	0.06	GHB-P024
	EC	1	0.36	0.12	99	20-30 cm height	0.15	(N79)
Brazil 1984	SR-Me	1	0.12	0.04	79	in bloom,	0.41	GHB-P024
	EC	1	0.36	0.12	79	50-60 cm height	0.45	(N79)
Brazil 1984	SR-Me	1	0.12	0.04	103	pre-bloom,	<0.05	GHB-P024
	EC	1	0.24	0.08	103	30 cm height	<0.05	(N79)
		1	0.36	0.12	103		0.05	
Brazil 1984	SR-Me	1	0.12	0.04	78	in bloom	0.15	GHB-P024

Country, Year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound, Form.	No	kg ai/ha	kg ai/hl				
	EC	1	0.24	0.08	78		0.35	(N79)
		1	0.36	0.12	78		0.52	
Brazil 1982	SR-Bt	1	0.06	0.02	110	4th	<0.05	GHB-P015
	EC	1	0.12	0.04	110	trifoliate,	<0.05	(N80D)
		1	0.18	0.06	110	20 cm height	<0.05	
		1	0.06[1]	0.02	110		<0.05	
		1	0.12[1]	0.04	110		<0.05	
		1	0.18[1]	0.06	110		<0.05	
Brazi 1982	SR-Bt	1	0.06	0.02	97	6th	<0.05	GHB-P015
	EC	1	0.12	0.04	97	trifoliate,	<0.05	(N80D)
		1	0.18	0.06	97	30 cm height	<0.05	
		1	0.06[1]	0.02	97		<0.05	
		1	0.12[1]	0.04	97		<0.05	
		1	0.18[1]	0.06	97		<0.05	
Brazil 1982	SR-Bt	1	0.12	0.04	142	4th	<0.05	GHB-P015
	EC	1	0.24	0.08	142	trifoliate,	<0.05	(N80D)
		1	0.12	0.04	142	20 cm height	0.06	
		1	0.24	0.08	142		0.06	
		1	0.12	0.04	142		<0.05	
		1	0.24	0.08	142		0.06	
		1	0.12	0.04	142		<0.05	
		1	0.24	0.08	142		0.06	
Brazil 1982	SR-Bt	1	0.12	0.036	132	8th	0.06	GHB-P015
	EC	1	0.24	0.072	132	trifoliate,	0.08	(N80D)
		1	0.12	0.036	132	45 cm height	0.07	
		1	0.24	0.072	132		0.08	
		1	0.12	0.036	132		<0.05	
		1	0.24	0.072	132		0.07	
		1	0.12	0.036	132		0.05	
		1	0.24	0.072	132		0.11	
Brazil	SR-Me	1	0.12	0.06	131	40 cm height	<0.05	GHB-P015
	EC	1	0.24	0.12	131		0.06	(N80D)
		1	0.36	0.18	131		0.06	
		1	0.48	0.24	131		0.8	
		1	0.3	0.15	131		<0.05	
		1	0.36	0.18	131		0.06	
USA 1983	SR-Me	1	0.28	N.S.[2]	84	in bloom	0.22	
					94	pre-bloom	0.067	(N73)
USA 1983	SR-Me	1	0.28	N.S.	86	in bloom	0.37	
					95	pre-bloom	0.11	(N73)
USA 1983	SR-Me	1	0.28	N.S.	69	in bloom	0.49	
					91	pre-bloom	0.023	(N73)

Country, Year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound, Form.	No	kg ai/ha	kg ai/hl				
USA 1983	SR-Me	1	0.28	N.S.	109	pre-bloom	0.2	(N73)
USA 1983	SR-Me	1	0.28	N.S.	82	in bloom	2.21	
					84	in bloom	2.06	(N73)
USA 1983	SR-Me	1	0.28	N.S.	90	in bloom	0.4	
					98	pre-bloom	0.06	(N73)
USA 1983	SR-Me	1	0.28	N.S.	89	in bloom	<0.05	
					122	pre-bloom	<0.05	(N73)
USA 1983	SR-Me	1	0.28	N.S.	106	in bloom	0.43	
					125	pre-bloom	0.05	(N73)
USA 1983	SR-Me	1	0.28	N.S.	69	in bloom	1.42	
					91	pre-bloom	0.21	(N73)
USA 1983	SR-Me	1	0.28	N.S.	86	in bloom	0.96	
					98	pre-bloom	0.3	(N73)
USA 1983	SR-Me	1	0.28	N.S.	73	in bloom	2.32	
								(N73)
USA 1983	SR-Me	1	0.28	N.S.	74	in bloom	3.08	
					86	in bloom	2	(N73)
USA 1983	SR-Me	1	0.28	N.S.	82	in bloom	1.24	
					96	pre-bloom	0.22	(N73)
USA 1983	SR-Me	1	0.28	N.S.	157	in bloom	0.16	
					167	pre-bloom	0.1	(N73)
USA 1983	SR-Me	1	0.28	N.S.	99	in bloom	0.34	
					127	pre-bloom	0.05	(N73)
USA 1983	SR-Me	1	0.28	N.S.	77	in bloom	0.25	
					118	pre-bloom	<0.05	(N73)
USA 1983	SR-Me	1	0.28	N.S.	75	in bloom	0.6	
					96	pre-bloom	0.08	(N73)
USA 1983	SR-Me	1	0.28	N.S.	76	in bloom	0.82	
					104	pre-bloom	0.08	(N73)
France 1990	R-Me	1	0.052	0.016	133	3 knots	<0.02	GHE-P-2515
	EC	1	0.1	0.032	133		<u><0.02</u>	(N81)
France 1990	R-Me	1	0.052	0.016	132	3 knots	<0.02	GHE-P-2515
	EC	1	0.1	0.032	132		<u><0.02</u>	(N81)
France 1990	R-Me	1	0.052	0.012	92	3-4 knots	0.04	GHE-P-2515
	EC				92		<0.05[3]	(N81)
		1	0.1	0.024	92		<u>0.07</u>	
					92		0.06[3]	
France 1990	R-Me	1	0.052	0.01	123	3 knots	<0.02	GHE-P-2515
	EC				123		<0.05[3]	(N81)
		1	0.1	0.021	123		<u><0.02</u>	
					123		<0.05[3]	
Italy 1989	R-Me	1	0.052	N.S.	76	6th trifoliate	0.05	GHE-P-2175
	EC	1	0.1	N.S.	76		<u>0.09</u>	(N80)

Country, Year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound, Form.	No	kg ai/ha	kg ai/hl				
Italy 1989	R-Me	2	0.039	N.S.	76	6th trifoliate	0.04	GHE-P-2175
	EC	2	0.078	N.S.	76		0.08	(N80)
Italy 1989	R-Me	1	0.052	N.S.	93	6th trifoliate	<0.02	GHE-P-2175
	EC	1	0.1	N.S.	93		<0.02	(N80)
Italy 1989	R-Me	2	0.039	N.S.	93	6th trifoliate	<0.02	GHE-P-2175
	EC	2	0.078	N.S.	93		<0.02	(N80)
Italy 1989	R-Me	1	0.052	N.S.	98	6-7th	<0.02	GHE-P-2175
	EC	1	0.1	N.S.	98	trifoliate	<0.02	(N80)
Italy 1989	R-Me	2	0.039	N.S.	93	6-7th	<0.02	GHE-P-2175
	EC	2	0.078	N.S.	93	trifoliate	<0.02	(N80)

[1] Spray included oil
[2] Not specified
[3] Straw

Potatoes. Twenty two supervised trials in Australia, Belgium, Germany, The Netherlands, Norway, Sweden and the UK with racemic haloxyfop-etotyl at 0.1-0.42 kg ai/ha with PHIs of 20-153 days, and twelve in Germany with haloxyfop-R-methyl at 0.1 kg ai/ha with PHIs of 2-123 days (Table 26).

Table 26. Residues of haloxyfop in potatoes. All single applications of EC formulation.

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Australia 1983	SR-EE	0.1	N.S.	147	7-10 true leaves	0.01	PAU-3313-159
		0.2	N.S.	147	30cm height	0.039	(N60B)
Belgium 1983	SR-EE	0.21	0.035	89	flowering	0.06	GHE-P-1226
		0.42	0.07	89		0.14	(N54)
Germany 1983	SR-EE	0.21	0.042	20	40 cm height,	0.02	GHE-P-1266
				30	first contact	0.02	(N55)
				55	with adjacent	0.01	
				62	plants	0.01	
				69		<0.01	
				83	normal harvest	<0.01	
The Netherlands 1982	SR-EE	0.21	0.035	96	N.S.[1]	0.03	GHE-P-1229 (N56)
The Netherlands 1983	SR-EE	0.21	N.S.	87		0.07	GHE-P-1228
		0.31	N.S.	87	30-35 cm	0.16	(N57)
		0.21	N.S.	93	height	0.05	
		0.31	N.S.	93		0.06	
Norway 1982	SR-EE	0.21	N.S.	89	4-5 cm height	0.02	GHE-P-1227
		0.42	N.S.	89		0.04	(N58)
Norway 1982	SR-EE	0.21	N.S.	77	10-15 cm	0.04	GHE-P-1227

		0.42	N.S.	77	height	0.11	(N58)
Norway 1982	SR-EE	0.21	N.S.	84	30 cm height	0.04	GHE-P-1227
		0.42	N.S.	84		0.1	(N58)
Norway 1982	SR-EE	0.21	N.S.	102	15-20 cm	0.05	GHE-P-1227
		0.42	N.S.	102	height	0.1	(N58)
Norway 1982	SR-EE	0.21	N.S.	71	10-15 cm	0.03	GHE-P-1227
		0.42	N.S.	71	height	0.05	(N58)
Norway 1983	SR-EE	0.21	N.S.	56	50 cm height	0.04	GHE-P-1225 (N59)
Norway 1983	SR-EE	0.21	N.S.	83	3-5 cm height	<0.01	GHE-P-1225 (N59)
Norway 1983	SR-EE	0.21	N.S.	89	25 cm height	0.01	GHE-P-1225 (N59)
Norway 1983	SR-EE	0.21	N.S.	104	0-5 cm height	<0.01	GHE-P-1225 (N59)
Sweden 1983	SR-EE	0.21	0.052	96	30 cm height	0.03	GHE-P-1224
		0.31	0.078	96		0.06	(N60)
UK 1982	SR-EE	0.21	N.S.	138	15-20 cm	0.04	GHE-P-1137
		0.42	N.S.	138	height	0.05	(N51)
UK 1982	SR-EE	0.1	N.S.	132	60 cm height	0.02	GHE-P-1137
		0.21	N.S.	132		0.04	(N51)
UK 1984	SR-EE	0.21	N.S.	153	13 cm height	0.01	GHE-P-1712
		0.42	N.S.	153		0.02	(N53)
		0.21	N.S.	133	40 cm height	0.07	
		0.42	N.S.	133		0.12	
UK 1984	SR-EE	0.21	N.S.	113		0.07	GHE-P-1712
		0.42	N.S.	113	50 cm height	0.11	(N53)
		0.21	N.S.	93		0.07	
		0.42	N.S.	93		0.11	
		0.21	N.S.	69		0.06	
		0.42	N.S.	69		0.08	
UK 1985	SR-EE	0.21	N.S.	115	30 cm height	0.1	GHE-P-1712
		0.42	N.S.	115		0.15	(N53)
UK 1985	SR-EE	0.1	N.S.	123		0.01	GHE-P-1712
		0.21	N.S.	123	20 cm height	0.03	(N53)
		0.42	N.S.	123		0.03	
UK 1985	SR-EE	0.1	N.S.	84	end of	<0.01	GHE-P-1712
		0.21	N.S.	84	flowering	0.01	(N53)
		0.42	N.S.	84		0.02	
		0.1	N.S.	56	senescing	0.06	
		0.21	N.S.	56		0.14	
		0.42	N.S.	56		0.16	
Germany 1988	R-Me	0.1	0.026	2	flowering complete	0.37	GHE-P-1977 (N50)
				42	mature	0.26	
Germany 1988	R-Me	0.1	0.026	13	bud formation beginning	0.33	GHE-P-1977 (N50)
				86	mature	0.1	

Germany 1988	R-Me	0.1	0.026	13	cover almost complete	0.36	GHE-P-1977 (N50)
				115	mature	0.06	
Germany 1988	R-Me	0.1	N.S.	6	first contact with adjacent plants	0.26	GHE-P-1977 (N50)
				42	mature	0.14	
Germany 1988	R-Me	0.1	N.S.	20	first contact with adjacent plants	0.2	GHE-P-1977 (N50)
				49	mature	0.1	
Germany 1988	R-Me	0.1	N.S.	20	first contact with adjacent plants	0.22	GHE-P-1977 (N50)
				90	mature	0.07	
Germany 1988	R-Me	0.1	N.S.	7	flowering complete	0.03	GHE-P-1977 (N50)
				42	mature	0.02	
Germany 1988	R-Me	0.1	N.S.	26	stem alongation	0.26	GHE-P-1977 (N50)
				102	mature	0.06	
Germany 1988	R-Me	0.1	N.S.	26	stem alongation	0.23	GHE-P-1977 (N50)
				118	mature	0.03	
Germany 1988	R-Me	0.1	N.S.	7	flowering complete	0.08	GHE-P-1977 (N50)
				42	mature	0.12	
Germany 1988	R-Me	0.1	N.S.	27	stem alongation	0.04	GHE-P-1977 (N50)
				114	mature	0.02	
Germany 1988	R-Me	0.1	N.S.	27	stem elongation	0.02	GHE-P-1977 (N50)
				123	mature	0.02	

[1] Not specified

Sugar beet. Forty two supervised trials in seven European countries were with racemic haloxyfop-etotyl at 0.1-0.83 kg ai/ha (mostly single treatments) with PHIs of 13-182 days. Eight supervised trials in France, Germany and Italy with haloxyfop-R-methyl were at 0.052-0.1 kg ai/ha with PHIs of 13-165 days. The residues of haloxyfop in the roots are shown in Table 27.

Table 27. Residues of haloxyfop in sugar beet (roots). All EC applications.

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
Belgium 1983	SR-EE	1	0.1	0.021	135	4 leaves	0.01	GHE-P-1222 (N13)
Denmark 1983	SR-EE	1	0.21	N.S.[1]	134	6 leaves	0.01	GHE-P-1263
		2	0.1	N.S.	118	8-10 leaves	0.04	(N14)
France 1982	SR-EE	1	0.1	N.S.	141		<0.03	GHE-P-994
		1	0.21	N.S.	141	2 leaves	<0.03	(N5)
		1	0.42	N.S.	141		<0.03	
France 1982	SR-EE	1	0.21	N.S.	120	2 leaves	<0.03	GHE-P-994

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
		1	0.42	N.S.	120		<0.03	(N5)
France 1982	SR-EE	1	0.21	N.S.	126	2 leaves	<0.03	GHE-P-994
		1	0.42	N.S.	126		<0.03	(N5)
France 1982	SR-EE	1	0.21	N.S.	128	2 leaves	0.05	GHE-P-994
		1	0.42	N.S.	128		0.08	(N5)
France 1982	SR-EE	1	0.1	N.S.	128		0.03	GHE-P-1049
		1	0.21	N.S.	128	2 leaves	0.1	(N9)
		1	0.42	N.S.	128		0.13	
France 1982	SR-EE	1	0.1	N.S.	120	2 leaves	0.01	GHE-P-1049 (N9)
France 1982	SR-EE	1	0.1	N.S.	126	2 leaves	0.01	GHE-P-1049 (N9)
France 1983	SR-EE	1	0.1	0.021	147		<0.01	GHE-P-1259
		1	0.21	0.042	147	7-8 leaves	<0.01	(N10)
		1	0.42	0.084	147		0.01	
		1	0.63	0.13	147		0.01	
France 1983	SR-EE	1	0.1	0.032	107		0.01	GHE-P-1259
		1	0.21	0.064	107	6-8 leaves	0.03	(N10)
		1	0.42	0.13	107		0.04	
France 1983	SR-EE	1	0.1	0.032	119		0.01	GHE-P-1259
		1	0.21	0.064	119	6-8 leaves	0.03	(N10)
		1	0.42	0.13	119		0.05	
France 1983	SR-EE	1	0.1	0.027	141		<0.01	GHE-P-1259
		1	0.21	0.053	141	8 leaves	0.02	(N10)
		1	0.42	0.11	141		0.05	
France 1988	SR-EE	1	0.1	0.042	131	2-3 leaves	<0.02	GHE-P-1972
		1	0.21	0.084	131		<0.02	(N10)
France 1988	SR-EE	1	0.1	N.S.	165	2 leaves	<0.02	GHE-P-1972
		1	0.21	N.S.	165		<0.02	(N10)
France 1988	SR-EE	1	0.1	N.S.	134	2 leaves	<0.02	GHE-P-1972
		1	0.21	N.S.	134		<0.02	(N10)
Germany 1982	SR-EE	1	0.21	0.052	21		0.15	GHE-P-1198
					87	N.S.	0.04	(N11)
					117		0.03	
					130	normal crop	0.01	
Germany 1982	SR-EE	1	0.21	0.042	82		0.02	GHE-P-1198
					118	N.S.	0.02	(N11)
					126	normal crop	0.02	

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
Germany 1983	SR-EE	1	0.21	0.052	89		<0.005	GHE-P-1198
					119	4-5 leaves	<0.005	(N11)
					150	normal crop	<0.005	
Germany 1983	SR-EE	1	0.1	0.021	37		0.04	GHE-P-1198
					71	N.S.	0.01	(N11)
					106		0.01	
					115	normal crop	0.02	
		1	0.21	0.042	37		0.06	
					71		0.04	
					106		0.01	
					115	normal crop	0.03	
Germany 1983	SR-EE	1	0.1	0.021	36		0.02	GHE-P-1198
					70	N.S.	0.01	(N11)
					101		0.01	
					114	normal crop	<0.01	
		1	0.21	0.042	36		0.03	
					70		0.02	
					101		0.01	
					114	normal crop	<0.01	
Germany 1988	SR-EE	1	0.21	0.052	13		0.38	GHE-P-2036
					76	6-8 leaves	0.16	(N11)
					104		0.06	
					118	normal crop	0.06	
Germany 1988	SR-EE	1	0.21	0.052	24		0.08	GHE-P-2036
					76	crop cover	0.14	(N11)
					108	complete	0.08	
					128	normal crop	0.05	
Germany 1988	SR-EE	1	0.21	0.052	15		0.25	GHE-P-2036
					98	6 leaves	0.01	(N11)
					125	normal crop	<0.01	
The Netherlands 1982	SR-EE	1	0.21	N.S.	137	8-10 leaves	0.04	GHE-P-1223 (N12)
Sweden 1982	SR-EE	1	0.21	0.1	119	6-8 leaves	0.01	GHE-P-1265
		1	0.21	0.1	126	6-10 leaves	0.02	(N15)
Sweden 1982	SR-EE	2	0.1	0.052	104	8-10 leaves	0.02	GHE-P-1265
					112		0.04	(N15)

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
Sweden 1982	SR-EE	2	0.21	0.1	133	6-10 leaves	0.04	GHE-P-1265
								(N15)
UK 1982	SR-EE	1	0.1	0.052	160	2-8 leaves	<0.03	GHE-P-993
		1	0.21	0.1	160		0.03	(N1)
UK 1982	SR-EE	1	0.21	0.1	168	2-8 leaves	<0.03	GHE-P-993
		1	0.42	0.21	168		<0.03	(N1)
UK 1982	SR-EE	1	0.21	0.1	181	2-8 leaves	0.03	GHE-P-993
		1	0.42	0.21	181		<0.03	(N1)
UK 1982	SR-EE	1	0.21	0.1	143		0.23	GHE-P-993
		1	0.21	0.1	181	2-8 leaves	0.06	(N1)
		1	0.42	0.21	143		0.15	
		1	0.42	0.21	181		<0.03	
UK 1982	SR-EE	1	0.21	N.S.	153	8 leaves	<0.01	GHE-P-1195
		1	0.42	N.S.	153		0.01	(N2)
UK 1982	SR-EE	1	0.21	0.1	180		0.01	GHE-P-1230
		1	0.42	0.21	180	6-8 leaves	0.01	(N3)
		1	0.83	0.42	180		0.02	
		1	0.21	0.1	143		0.06	
		1	0.42	0.21	143	10-12 leaves	0.09	
		1	0.83	0.42	143		0.25	
UK 1982	SR-EE	1	0.21	0.1	168		0.01	GHE-P-1230
		1	0.42	0.21	168	4-6 leaves	0.02	(N3)
		1	0.83	0.42	168		0.01	
		1	0.21	0.1	153		0.04	
		1	0.42	0.21	153	11 leaves	0.04	
		1	0.83	0.42	153		0.06	
UK 1982	SR-EE	1	0.21	0.1	181		<0.01	GHE-P-1230
		1	0.42	0.21	181	4-6 leaves	<0.01	(N3)
		1	0.83	0.42	181		0.02	
		1	0.21	0.1	166		0.02	
		1	0.42	0.21	166	12 leaves	0.05	
		1	0.83	0.42	166		0.13	
UK 1983	SR-EE	1	0.21	0.1	135		0.04	GHE-P-1262
		1	0.42	0.21	135	6-8 leaves	0.08	(N4)
		1	0.21	0.1	135		0.05	
		1	0.42	0.21	135		0.07	

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
UK 1983	SR-EE	1	0.21	0.1	117	10-12 leaves	0.04	GHE-P-1262
		1	0.42	0.21	117		0.05	(N4)
UK 1984	SR-EE	1	0.21	0.1	38	mature	0.1	GHE-P-1310
					68	rows meeting	0.16	(N6)
					94	30 cm height	0.05	
					124	8-10 leaves	0.02	
					147	4 leaves	<0.01	
					174	cotyledon	<0.01	
		1	0.42	0.21	38		0.16	
					68		0.3	
					94		0.1	
					124		0.03	
					147		<0.01	
					174		<0.01	
		1	0.63	0.31	38		0.25	
					68		0.45	
					94		0.14	
					124		0.04	
					147		<0.01	
					174		<0.01	
UK 1984	SR-EE	1	0.21	0.1	28	mature	0.08	GHE-P-1314
					60	mature	0.09	(N7)
					97	40-50 cm height	0.1	
					126	10-12 cm height	0.05	
					153	4-6 leaves	0.05	
		1	0.42	0.21	28		0.15	
					60		0.16	
					97		0.16	
					126		0.1	
					153		0.08	
		1	0.63	0.31	28		0.21	
					60		0.23	
					97		0.26	
					126		0.2	
					153		0.02	

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
UK 1984	SR-EE	1	0.21	0.1	43	mature	0.12	GHE-P-1314
					78	18-26 leaves	0.13	(N7)
					106	11 leaves	0.07	
					146	11 leaves	0.03	
					163	6 leaves	<0.01	
		1	0.42	0.21	43		0.15	
					78		0.23	
					106		0.12	
					146		0.04	
					163		0.02	
		1	0.62	0.31	43		0.22	
					78		0.33	
					106		0.17	
					146		0.06	
					163		0.02	
UK 1984	SR-EE	1	0.21	0.1	63	mature	0.07	GHE-P-1314
					98	28-30 leaves	0.15	(N7)
					125	25-30 leaves	0.13	
					166	9 leaves	0.02	
					182	4 leaves	<0.01	
		1	0.42	0.21	63		0.14	
					98		0.14	
					125		0.22	
					166		0.04	
					182		<0.01	
		1	0.62	0.31	63		0.15	
					98		0.12	
					125		0.23	
					166		0.05	
					182		<0.01	
France 1988	R-Me	1	0.052	0.021	131	2-3 leaves	<0.02	GHE-P-1972
		1	0.1	0.042	131		<0.02	(N10)
France 1988	R-Me	1	0.052	N.S.	165	2 leaves	<0.02	GHE-P-1972
		1	0.1	N.S.	165		<0.02	(N10)
France 1988	R-Me	1	0.052	N.S.	134	2 leaves	<0.02	GHE-P-1972
		1	0.1	N.S.	134		<0.02	(N10)
Germany 1988	R-Me	1	0.1	0.026	13		0.3	GHE-P-2036

haloxyfop

Country, year	Application				PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	No.	kg ai/ha	kg ai/hl				
					76	6-8 leaves	0.06	(N11)
					104		0.05	
					118	normal crop	0.04	
Germany 1988	R-Me	1	0.1	0.026	24	crop cover	0.22	GHE-P-2036
					76	complete	0.03	(N11)
					108		0.04	
					128	normal crop	0.03	
Germany 1988	R-Me	1	0.1	0.026	15	6 leaves	0.11	GHE-P-2036
					98		0.01	(N11)
					125	normal crop	<0.01	
Italy 1992	R-Me	1	0.1	0.026	67	8-9 leaves	0.03	GHE-P-3078 (N13)
Italy 1992	R-Me	1	0.1	0.026	65	8-9 leaves	0.02	GHE-P-3078 (N13)

[1] Not specified

Cereals

Rice. Nine supervised trials in Brazil, Colombia, Costa Rica and Mexico with racemic haloxyfop-methyl at 0.03-10.24 kg ai/ha. Residues in husked rice, polished rice and rice bran were below the LOD (<0.01 or <0.02 mg/kg) at PHIs of 89-140 days (Tables 28 and 29).

Table 28. Residues of haloxyfop in husked rice. All single EC applications of racemic haloxyfop-methyl.

Country, year	Application		PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	kg ai/ha	kg ai/hl				
Brazil 1986	0.06	0.02	131	22 days	<0.01	GHB-P050
	0.09	0.03	131	after	<0.01	(N128)
	0.12	0.04	131	planting	<0.01	
	0.15	0.05	131	2-5 tillers	<0.01	
	0.18	0.06	131		<0.01	
	0.24	0.08	131		<0.01	
Brazil 1987	0.03	0.01	98	25 days after planting	<0.01	GHB-P050
	0.06	0.02	98	1-2 tillers	<0.01	(N128)
	0.12	0.04	98		<0.01	
Colombia 1985	0.06	0.038	118	26 days	<0.01	GHB-P025
	0.09	0.057	118	after	<0.01	(N130B)
	0.12	0.076	118	planting	<0.01	
	0.15	0.095	118		<0.01	
Mexico 1986	0.075	N.S.[1]	123	24 days	<0.01	GHB-P048
	0.09	N.S.	123	after	<0.01	(N127)
	0.12	N.S.	123	planting	<0.01	
Mexico 1985	0.04	N.S.	118	22 days	<0.01	GHB-P033
	0.08	N.S.	118	after	<0.01	(N130A)
	0.12	N.S.	118	planting	<0.01	
Mexico 1985	0.04	N.S.	122	12 days	<0.01	GHB-P033
	0.08	N.S.	122	after	<0.01	(N130A)
	0.12	N.S.	122	planting	<0.01	
Mexico 1985	0.08	N.S.	124	25 days	<0.01	GHB-P033
	0.12	N.S.	124	after planting	<0.01	(N130A)

[1] Not specified

Table 29. Residues of haloxyfop in polished rice and rice bran from single EC applications of racemic haloxyfop-methyl in Coasta Rica, 1985.

Application		PHI, days	Growth stage at last treatment	Residues, mg/kg		Reference
kg ai/ha	kg ai/hl			Polished rice	Bran	
0.06	0.03	118	22 days	<0.01	<0.02	GHB-P029
0.09	0.045	118	after planting	<0.01	<0.02	(N130D)
0.06	0.03	131	19 days	<0.01	<0.02	GHB-P030
0.06	0.03	140	after planting	<0.01	<0.02	(N130C)

Oil seeds

Cotton seed. Four supervised trials were carried out in Australia with racemic haloxyfop-etotyl at 0.16-0.37 kg ai/ha, and four in Brazil with racemic haloxyfop-methyl at 0.12-0.48 kg ai/ha. PHIs were 93-162 days. A single trial in Spain with haloxyfop-R-methyl at 0.16 kg ai/ha gave residues of <0.02 mg/kg at a PHI of 123 days (Table 30).

Table 30. Residues of haloxyfop in cotton seed. All single EC applications.

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Australia 1986	SR-EE	0.16	N.S.[1]	123	flowering	0.06	
		0.31	N.S.	123		0.08	(N111)
	SR-EE	0.16	N.S.	97	flower + squares	<0.05	(N111)
Australia		0.2	N.S.	162	1 leaf	<0.05	
1986		0.31	N.S.	97		<0.05	
		0.37	N.S.	162		<0.05	
	SR-EE	0.16	N.S.	94	flowering	<0.05	(N111)
Australia				135	6-7 leaves	<0.05	
1986				157	2-6 leaves	<0.05	
		0.31	N.S.	94		<0.05	
				135		<0.05	
				157		<0.05	
	SR-EE	0.16	N.S.	113	flower + squares	0.08	(N111)
Australia				142	6-8 leaves	<0.05	
1986				157	2-6 leaves	<0.05	
		0.31	N.S.	113		0.1	
				142		<0.05	
				157		<0.05	
	SR-Me	0.12	0.032	112	40 days after	<0.1	GHB-P034
Brazil		0.24	0.065	112	planting	<0.1	(N113)
1984		0.36	0.097	112		<0.1	
	SR-Me	0.12	0.033	111	40 days after	<0.1	GHB-P034

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Brazil		0.24	0.066	111	planting	<0.1	(N113)
1983		0.36	0.1	111		<0.1	
	SR-Me	0.12	0.04	101	23 days after	<0.1	GHB-P034
Brazil		0.24	0.08	101	planting	0.1	(N113)
1985		0.36	0.12	101		0.1	
		0.48	0.16	101		0.1	
	SR-Me	0.12	0.04	93	22 days after	0.1	GHB-P034
Brazil		0.24	0.08	93	planting	0.2	(N113)
1985		0.36	0.12	93		0.2	
		0.48	0.16	93		0.3	
Spain 1991	R-Me	0.16	0.052	123	8 leaves	<0.02	GHE-P-2802 (N150)

[1] Not specified

Peanuts. Six supervised trials in Argentina and Australia with 0.05-0.48 kg ai/ha of racemic haloxyfop esters with PHIs of 76-141 days (Table 31).

Table 31. Residues of haloxyfop in peanuts. All single EC applications.

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Argentina 1990	SR-Me	0.12	0.06	141	28 days after	<0.05	GHB-P110R
		0.24	0.12	141	planting	<0.05	(N125A)
		0.48	0.24	141		<0.05	
Argentina 1983	SR-EE	0.05	0.075	114	N.S.[1]	<0.01	PAU-3312-186
		0.1	0.15	114		0.03	(N121)
		0.4	0.6	114		0.03	
Australia 1983	SR-EE	0.05	0.075	115	N.S.	<0.01	PAU-3312-189
		0.1	0.15	115		0.01	(N122)
		0.4	0.6	76		0.22	
Australia 1985	SR-Me	0.058	0.029	98	N.S.	0.02	PAU-3313-197
		0.12	0.058	98		0.03	(N123)
		0.23	0.12	98		0.03	
Australia 1986	SR-EE	0.16	0.14	82	first peanuts present	0.05	PAU-3313-252
				103	15-18 cm height, flowers present	0.03	(N124)
				117	8-9th trifoliate	0.03	

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
		0.31	0.29	82		0.08	
				103		0.07	
				117		0.06	
Australia 1986	SR-EE	0.16	0.14	84	first peanuts present	<0.03	PAU-3313-252
				97	30 cm height, flowering	<0.03	(N124)
				113	7th trifoliate	<0.03	
		0.31	0.29	84		<0.03	
				97		<0.03	
				113		<0.03	

[1] Not specified

Rape seed. Many supervised trials in Australia, France, Germany, Norway, Sweden and the UK with 0.078-0.63 kg ai/ha of racemic haloxyfop-etotyl with PHIs of 69-328 days. Five trials in France and Germany were with haloxyfop-R-methyl at 0.052-0.1 kg ai/ha with PHIs of 248-272 days (Table 32).

Table 32. residues of haloxyfop in rape seed. All single applications of EC formulation.

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Australia 1986	SR-EE	0.078	0.078	119	6 leaves	0.04	PAU-3313-263
				134	5 leaves	<0.03	(N36)
				160	2 leaves	<0.03	
		0.16	0.16	119		0.07	
				134		<0.03	
				160		<0.03	
Australia 1986	SR-EE	0.078	0.078	69	30 cm height	0.54	PAU-3313-263
				110	2 leaves	<0.03	(N36)
		0.16	0.16	69		1.42	
				110		<0.03	
France 1989	SR-EE	0.1	0.042	268	8 leaves	<0.05	GHE-P-1973
		0.21	0.084	268	(Autumn)	<0.05	(N1)
France 1989	SR-EE	0.1	N.S.[1]	248	4-5 leaves	<0.05	GHE-P-1973
		0.21	N.S.	248	(Autumn)	<0.05	(N1)
France 1989	SR-EE	0.1	N.S.	261	4-5 leaves	<0.05	GHE-P-1973
		0.21	N.S.	261	(Autumn)	<0.05	(N1)
France 1982	SR-EE	0.16	0.031	201	60 days after	0.05	GHE-P-996 (N26)
		0.21	0.042	201	planting	0.05	
		0.26	0.052	201	(Autumn)	0.04	GHE-P-1047 (N27)

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
France 1982	SR-EE	0.16	0.052	164	4 months	0.125	GHE-P-996
		0.21	0.07	164	after	0.145	(N26)
		0.42	0.14	164	planting	0.315	GHE-P-1047
					(February)		(N27)
France 1983	SR-EE	0.1	0.026	122	5 months	0.28	GHE-P-1048
		0.21	0.052	122	after	0.37	(N28)
		0.42	0.1	122	planting	0.83	
		0.1	0.021	119		0.4	
		0.21	0.042	119	(March)	0.66	
		0.42	0.083	119		1.68	
France 1983	SR-EE	0.1	0.021	221	75 days after	0.06	GHE-P-1048
		0.21	0.042	221	planting	0.09	(N28)
		0.42	0.083	221	(Autumn)	0.17	
France 1983	SR-EE	0.1	0.026	227	55 days after	<0.05	GHE-P-1048
		0.21	0.052	227	planting	<0.05	(N28)
		0.42	0.1	227	(Autumn)	0.05	
France 1983	SR-EE	0.1	0.039	234	50 days after	<0.05	GHE-P-1048
		0.21	0.077	234	planting	<0.05	(N28)
		0.42	0.15	234	(Autumn)	0.05	
France 1983	SR-EE	0.1	0.021	150	5 months after planting (February)	<0.05	GHE-P-1196
		0.21	0.042	150		<0.05	(N29)
		0.42	0.084	150		<0.05	
France 1982	SR-EE	0.21	0.069	164	4-5 leaves	0.14	GHE-P-1050R (N30)
		0.42	0.14	164	(February)	0.32	
France 1983	SR-EE	0.1	0.026	227	5-6 leaves	<0.05	GHE-P-1313R (N31)
		0.21	0.052	227	(Autumn)	<0.05	
France 1983	SR-EE	0.1	0.026	122	beginning of spring growth (March)	0.28	GHE-P-1313R (N31)
		0.21	0.052	122		0.37	
Germany 1989	SR-EE	0.21	0.052	272	6 leaves (Autumn)	0.13	GHE-P-2144 (N2)
Germany 1989	SR-EE	0.21	0.052	259	6 leaves (Autumn)	<0.05	GHE-P-2144 (N2)
Germany 1982	SR-EE	0.16	0.04	95	7 mo after planting (April)	0.29	GHE-P-1194R (N32)
Germany 1982	SR-EE	0.16	N.S.	106	7 mo after planting (April)	0.14	GHE-P-1194R
		0.21	N.S.	106		0.1	(N32)
Germany 1983	SR-EE	0.16	N.S.	259	57 days after planting	<0.05	GHE-P-1194R (N32)

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
					(Autumn)		
		0.21	N.S.	99	7 mo after planting (April)	0.77	
Germany 1982	SR-EE	0.16	0.031	303	46 days after planting (Autumn)	<0.05	GHE-P-1194R (N32)
Germany 1983	SR-EE	0.1	0.021	107	8 mo after planting (April)	0.11	GHE-P-1194R
		0.21	0.042	107		0.13	(N32)
Germany 1982	SR-EE	0.1	0.021	116	7 mo after planting (March)	0.05	GHE-P-1194R
		0.21	0.042	116		0.15	(N32)
Germany 1983	SR-EE	0.16	0.031	301	36 days after planting (Autumn)	<0.05	GHE-P-1194R (N32)
Germany 1983	SR-EE	0.16	N.S.	289	33 days after	<0.05	GHE-P-1311
					planting		(N33)
					(Autumn)		
Germany 1983	SR-EE	0.16	N.S.	313	4 leaves (Autumn)	0.06	GHE-P-1311 (N33)
Norway 1983	SR-EE	0.21	N.S.	70	4-5 leaves (June)	1.49	GHE-P-1219 (N35)
Norway 1983	SR-EE	0.21	N.S.	79	4-5 leaves (June)	0.91	GHE-P-1219 (N35)
Norway 1983	SR-EE	0.21	N.S.	80	15-20 cm height (July)	2.13	GHE-P-1219 (N35)
Norway 1983	SR-EE	0.21	N.S.	85	5-10 cm height (June)	<0.05	GHE-P-1219 (N35)
Sweden 1982	SR-EE	0.1	0.026	85	18-20 cm	0.58	GHE-P-1220
		0.21	0.052	85	height	1.2	(N34)
		0.42	0.1	85	(June)	2.64	
UK 1982	SR-EE	0.12	0.06	237	64 days after planting (Autumn)	<0.05	GHE-P-995 (N21)
UK 1982	SR-EE	0.12	0.06	244	3 mo after planting (Autumn)	<0.05	GHE-P-995 (N21)
UK 1982	SR-EE	0.12	0.06	264	1 mo after planting (Autumn)	<0.05	GHE-P-995 (N21)

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
UK 1982	SR-EE	0.12	0.03	270	2 mo after planting (Autumn)	<0.05	GHE-P-995 (N21)
UK 1982	SR-EE	0.3	0.15	229	2 mo after planting (Autumn)	0.05	GHE-P-995 (N21)
UK 1982	SR-EE	0.3	0.15	235	3 mo after planting (Autumn)	<0.05	GHE-P-995 (N21)
UK 1982	SR-EE	0.3	0.15	270	39 days after planting (Autumn)	<0.05	GHE-P-995 (N21)
UK 1983	SR-EE	0.21	0.1	292	4-6 leaves	<0.05	GHE-P-1221
		0.42	0.21	292	(Autumn)	<0.05	(N22)
UK 1983	SR-EE	0.21	0.1	292	4-6 leaves	<0.05	GHE-P-1221
		0.42	0.21	292	(Autumn)	<0.05	(N22)
UK 1983	SR-EE	0.21	0.1	292	4-6 leaves	<0.05	GHE-P-1221
		0.42	0.21	292	(Autumn)	<0.05	(N22)
UK 1983	SR-EE	0.21	0.1	279	4-6 leaves	<0.05	GHE-P-1221
		0.42	0.21	279	(Autumn)	<0.05	(N22)
UK 1983	SR-EE	0.21	0.1	279	4-6 leaves	<0.05	GHE-P-1221
		0.42	0.21	279	(Autumn)	<0.05	(N22)
UK 1983	SR-EE	0.21	0.1	279	4-6 leaves	<0.05	GHE-P-1221
		0.42	0.21	279	(Autumn)	<0.05	(N22)
UK 1983	SR-EE	0.21	0.1	269	4-5 leaves	<0.05	GHE-P-1267
		0.42	0.21	269	(Autumn)	<0.05	(N23)
UK 1983	SR-EE	0.21	0.1	292	5 leaves	<0.05	GHE-P-1267
		0.42	0.21	292	(Autumn)	<0.05	(N23)
UK 1983	SR-EE	0.21	0.1	265	3-4 leaves	<0.05	GHE-P-1264
		0.42	0.21	265	(Autumn)	<0.05	(N24)
		0.21	0.1	158	7 leaves	0.05	
		0.42	0.21	158	(March)	0.06	
UK 1983	SR-EE	0.21	0.1	265	3-4 leaves	<0.05	GHE-P-1264
		0.42	0.21	265	(Autumn)	<0.05	(N24)
		0.21	0.1	158	7 leaves	0.06	
		0.42	0.21	158	(March)	0.08	
UK 1984	SR-EE	0.21	0.1	85	early flowering (May)	3.32	GHE-P-1312
				113	buds appearing (April)	1.62	(N25)
				142	spring growth (March)	0.42	
				167	spring growth (Feb.)	0.44	
				199	8 leaves (Jan.)	0.13	
				248	6 leaves (Autumn)	0.09	

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
				272	4-5 leaves (Autumn)	0.08	
		0.42	0.21	85		3.94	
				113		3.05	
				142		1.05	
				167		0.6	
				199		0.26	
				248		0.09	
				272		0.09	
		0.63	0.31	85		5.64	
				113		2.69	
				142		1.04	
				167		0.64	
				199		0.36	
				248		0.13	
				272		0.1	
UK 1984	SR-EE	0.21	0.1	83	full flower (May)	2.68	GHE-P-1312
				111	35-40 cm height (April)	1.98	(N25)
				140	9 leaves (March)	0.64	
				171	6 leaves (Feb)	0.17	
				234	6 leaves (Autumn)	0.08	
				259	6 leaves (Autumn)	0.11	
				287	5 leaves (Autumn)	0.11	
		0.42	0.21	83		5.31	
				111		2.78	
				140		0.87	
				171		0.11	
				234		0.12	
				259		0.24	
				287		0.22	
		0.63	0.31	83		7.57	
				111		4.37	
				140		1.06	
				171		0.33	
				234		0.17	
				259		0.26	
				287		0.21	
UK 1984	SR-EE	0.21	0.1	131	flowering (May)	2.49	GHE-P-1312
				153	11 leaves (April)	0.42	(N25)
				177	7 leaves (March)	0.1	
				208	7 leaves (Feb)	<0.05	
				280	7 leaves (Autumn)	<0.05	
				302	7 leaves (Autumn)	<0.05	
				328	5 leaves (Autumn)	<0.05	
		0.42	0.21	131		2.63	GHE-P-1312

Country, year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
				153		0.78	(N25)
				177		0.26	
				208		0.07	
				280		<0.05	
				302		<0.05	
				328		<0.05	
		0.63	0.31	131		5.35	GHE-P-1312
				153		1.29	(N25)
				177		0.28	
				208		0.09	
				280		<0.05	
				302		<0.05	
				328		<0.05	
France 1989	R-Me	0.052	0.021	268	8 leaves	<0.05	GHE-P-1973
		0.1	0.042	268	(Autumn)	<0.05	(N1)
France 1989	R-Me	0.052	N.S.	248	4-5 leaves	<0.05	GHE-P-1973
		0.1	N.S.	248	(Autumn)	<0.05	(N1)
France 1989	R-Me	0.052	N.S.	261	4-5 leaves	<0.05	GHE-P-1973
		0.1	N.S.	261	(Autumn)	<0.05	(N1)
Germany 1989	R-Me	0.1	0.026	272	6 leaves (Autumn)	0.07	GHE-P-2144 (N2)
Germany 1989	R-Me	0.1	0.026	259	6 leaves (Autumn)	<0.05	GHE-P-2144 (N2)

[1] Not specified

Sunflower seed. Eight supervised trials in Argentina, Australia and France at 0.078-0.78 kg ai/ha of racemic haloxyfop with PHI of 60-155 days. One supervised trial was carried out in France at 0.052-0.1 kg ai/ha of haloxyfop-R-methyl with PHI of 89-118 days (Table 33).

Table 33. Residues of haloxyfop in sunflower seed. All single EC applications.

Country Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Argentina 1982	SR-Me	0.36	0.18	67	50-70 cm	0.14	GHB-P017
		0.78	0.25	60	height	0.25	(N44)
Australia 1985	SR-EE	0.078	0.072	94	seedling	<0.01	PAU-3313-196
		0.1	0.095	94		<0.01	(N45)
		0.16	0.14	94		0.03	
		0.31	0.29	94		0.04	
Australia 1986	SR-EE	0.16	0.21	122	2 leaves	<0.03	PAU-3313-238
		0.31	0.42	122		<0.03	(N49)
		0.16	0.062	111	6 leaves	<0.03	
		0.31	0.125	111		0.04	
Australia 1986	SR-EE	0.16	0.16	84	15 leaves	0.04	PAU-3313-146
		0.31	0.32	84		0.06	(N50)
France 1982	SR-EE	0.1	0.026	155	40 days after	<0.05	GHE-P-997
		0.21	0.052	155	planting	<0.05	(N41)
		0.42	0.1	155		<0.05	
France 1982	SR-EE	0.1	0.026	155	40 days after	<0.05	GHE-P-1046
		0.21	0.052	155	planting	<0.05	(N42)
		0.42	0.1	155		<0.05	
France 1989	SR-EE	0.1	0.031	89	8 pairs of leaves	0.05	GHE-P-2059
				105	6 pairs of leaves	<0.05	(N20)
				118	3 pairs of leaves	<0.05	
		0.21	0.062	89		0.16	
				105		0.07	
				118		0.09	
France 1989	R-Me	0.052	0.016	89	8 pairs of leaves	<0.05	GHE-P-2059
				105	6 pairs of leaves	<0.05	(N20)
				118	3 pairs of leaves	<0.05	
		0.1	0.031	89		0.07	
				105		<0.05	

Country Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
				118		<0.05	

Animal feeds

Alfalfa. Five supervised trials in Australia with 0.1-0.31 kg ai/ha of racemic haloxyfop-etotyl (PHIs 4-42 days) and two with 0.052-0.1 kg ai/ha of haloxyfop-R-methyl with PHIs of 8-32 days (Table 34).

Table 34. Residues of haloxyfop in alfalfa in Australia. All single EC applications.

Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
1984	SR-EE	0.2	0.2	42	N.S.	3.71	PAU-3312-191 (N126)
1989	SR-EE	0.1	0.11	8	N.S.	3.08	GHF-P925
				14		2.77	(N126A)
				22		1.49	
				32		1.13	
		0.21	0.21	8		8.41	
				14		6.45	
				22		2.45	
				32		1.34	
1989		0.1[1]	0.11	8		3.61	GHF-P925
				14		4.44	
				22		3.36	
				32		1.86	
1988	SR-EE	0.1	0.1	4	N.S.	4.56	GHF-P857
				7		4.68	(N126D)
				14		2.48	
				21		2.11	
		0.21	0.21	4		8.35	
				7		8.15	
				14		3.09	
				21		3.11	
		0.31	0.31	4		11.8	
				7		10.1	
				14		5.94	
				21		2.93	
1989	SR-EE	0.1[1]	0.11	8	N.S.	3.61	GHF-P-1355
				14		4.44	(N126C)
				22		3.36	
				32		1.86	
1989	R-Me	0.052	0.053	8	N.S.	1.3	GHF-P997

Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
				14		1.3	(N126B)
				22		0.8	
				32		0.7	
		0.1	0.11	8		3.2	
				14		2.4	
				22		1.8	
				32		1.9	
1989	R-Me	0.052	0.053	8		1.58	GHF-P-1355
				14		1.93	(N126C)
				22		1.6	
				32		1.01	
		0.1	0.11	8		3.52	
				14		3.42	
				22		2.21	
				32		1.94	

[1] Spray solution containing oil

Bean fodder and foliage. The results of six supervised trials were submitted: five with haloxyfop-R-methyl and one with racemic haloxyfop-etotyl (Table 35).

Table 35. Residues of haloxyfop in field bean fodder and foliage. All single EC application.

Country	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
UK 1991	SR-EE	0.21	N.S.[1]	104	end of	0.18	GHE-P-2654
		0.42	N.S.	104	flowering	0.34	(N65)
Germany 1989	R-Me	0.1	0.035	0	4 leaves	2.67[2]	GHE-P-2155
				35		0.03[2]	(N35)
				55		<0.02[2]	
				89		<0.05	
Germany 1989	R-Me	0.1	0.035	0	4 leaves	4.19[2]	GHE-P-2155
				30		0.05[2]	(N35)
				46		0.02[2]	
				91		<0.05	
Germany 1989	R-Me	0.1	0.026	1	6 leaves	4.65[2]	GHE-P-2155
				36		0.06[2]	(N35)
				71		0.02[2]	
				120		<0.05	
Germany 1989	R-Me	0.1	0.026	1	6 leaves	0.63[2]	GHE-P-2155

				17		0.13[2]	(N35)
				42		0.02[2]	
				105		<0.05	
UK 1991	R-Me	0.1	N.S.	104	end of	0.12	GHE-P-2654
		0.21	N.S.	104	flowering	0.16	(N38)

[1] Not specified
[2] Whole plant

Pea fodder and foliage. The results of six supervised trials were submitted, five with haloxyfop-R-methyl and one with the racemic ethoxyethyl ester (Table 36).

Table 36. Residues of haloxyfop in pea hay or fodder. All single EC applications.

Crop, Country, Year	Application			PHI, days	Growth stage at last treatment	Residues, mg/kg	Reference
	Compound	kg ai/ha	kg ai/hl				
Peas Germany 1989	R-Me	0.1	0.035	0 43 56 56 76	3 leaves	2.92[1] <0.02[1] <0.02[2] <0.02[3] <0.02[3]	GHE-P-2154 (N36)
Peas Germany 1989	R-Me	0.1	0.035	0 38 53 53 77	4 leaves	4.3[1] 0.03[1] <0.02[2] <0.02[3] 0.05[3]	GHE-P-2154 (N36)
Peas Germany 1989	R-Me	0.1	0.026	1 20 42 60	10 leaves	1.13[1] 0.39[1] 0.12[3] <0.05[3]	GHE-P-2154 (N36)
Peas Germany 1989	R-Me	0.1	0.026	1 42 60 80	6-7 leaves	0.47[1] <0.02[1] <0.02[3] <0.05[3]	GHE-P-2154 (N36)
Pigeon peas Australia 1989	SR-EE	0.16 0.31	0.14 0.28	14 28 56 14 28 56	43 days after planting	2.59[1] 1.53[1] 0.48[1] 6.65[1] 3.14[1] 1.3[1]	GHF-P-941 (N70B)
Pigeon peas Australia 1989	R-Me	0.038 0.075	0.035 0.068	14 28 56 14 28 56	43 days after planting	1.83[1] 0.41[1] 0.13[1] 1.44[1] 1.00[1] 0.21[1]	GHF-P-941 (N70B)

[1] Whole plant CLICK HERE to continue

METALAXYL (138)

EXPLANATION

Metalaxyl was first evaluated in 1982 and has been reviewed several times since, most recently in 1989, 1990 and 1992. At the 1994 CCPR the delegations of France and Germany and the EEC representative questioned the underlying data for the maximum residue level of 0.2 mg/kg in strawberries estimated by the 1992 JMPR (ALINORM 95/24, para 252). The EEC representative stated that the European Union is currently considering an MRL of 0.5 mg/kg for strawberry so the proposal of 0.2 mg/kg would not cover all uses. This was confirmed by the delegation of the USA. The MRL was held at step 7B pending review by the 1995 JMPR.

Since metalaxyl has been proposed for periodic review the Meeting considered only the MRL for strawberry. Information on GAP for other commodities received from Australia, Germany, The Netherlands, Peru and the UK and monitoring data provided by Australia will be kept on file and considered by a future JMPR as part of the periodic review.

The manufacturer provided updated information on GAP, eight new residue reports and an overall assessment of the residue situation for strawberries (Leuthold, 1995). Summaries of information on GAP for strawberries have been provided by Australia (Anon., 1995a), the UK (Anon., 1994a), The Netherlands (Anon., 1994b) and Canada (Anon., 1995b). Information on analytical methods and residue data (Dornseiffen *et al*., 1989a,b) was also made available by The Netherlands.

METHODS OF RESIDUE ANALYSIS

After extraction with dichloromethane, evaporation of the solvent and solution in n-hexane, the quantitative determination of the parent compound metalaxyl has been carried out by GLC with a nitrogen-specific detector (LOD 0.04 mg/kg). Metalaxyl and its metabolites containing 2,6-dimethylaniline have been determined by the same means (LOD 0.03 mg/kg) after extraction with dichloromethane, partitioning into water, acid hydrolysis of metalaxyl and the metabolites to 2,6-dimethylaniline, and bromination to 4-bromo-2,6-dimethylaniline (Anon., 1995b; Dornseiffen *et al*., 1989a,b).

USE PATTERN

The use of metalaxyl on strawberries is registered world-wide. Detailed information is shown in Table 1. Metalaxyl is applied by foliar spray, as a soil drench, soil spread with incorporation, or by dipping plants before planting. The PHI depends on local conditions and varies over a wide range. The critical GAP can be defined as follows.

Foliar spray: 0.7 kg ai/ha and a PHI of 30 days (France)
Broadcast: 2 kg ai/ha and a PHI of 40 days (Italy)
Soil incorporation: 3 kg ai/ha, at planting, no PHI (Japan)
Soil drench: 1.2 kg ai/ha and a PHI of 14 days (Mexico, UK).

Table 1. Registered uses of metalaxyl on strawberries.

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

Country	Form	Application				PHI, days
		Method	kg ai/ha	kg ai/hl	No.	
Australia	WP	dipping		0.008		
Austria	GR	soil spread before planting	0.5		1	
Belgium	WP	dipping and pouring or spraying (plantation)	0.3		1-2	60
	GR	soil	0.75		2	60
Canada	EC	spray (autumn)	1		2	
	EC	spray post-planting and again in autumn	2.04		1-2	
Chile	GR	soil, 1st post-harvest, 2nd in spring	0.5-1		2	14
Finland	WP	drench of seedlings	0.05[1]	0.024	1	
France	WP	soil drench	0.7-1		1	30
	WP	soil drench end of growing period	0.7		2	30
	SC	foliar spray end of growing period	0.7		2	30
Italy	WP	foliar spray post-planting	0.2		2	40
	GR	broadcast or incorp. into soil pre-transplanting	2		1	40
Japan	GR	soil incorp.	3		1	
Malaysia	GR	broadcast at planting	0.5-1		1	
Mexico	EC	soil	1.2		2	14
Netherlands	GR	spread or row treatment	0.38		1-2	42
Romania	WP	foliar		0.032		40
Spain	GR	soil spread before planting	0.5-1		1	
UK	WP	soil drench after planting	1.24		1	14
USA[2]	EC or WP	ground, drip irrigation	1.12		2-3	

[1] l/plant (corresp. to approx. 1.2 kg ai/ha)
[2] incomplete information on GAP submitted

RESIDUES RESULTING FROM SUPERVISED TRIALS

New data from supervised trials were provided by the manufacturer.

Six studies were carried out in Spain (Kühne, 1994a-f; report nos. 2057/93-2062/93) with three sprayings at two-week intervals at 0.35 kg ai/ha. Fruit were sampled 7, 14 and 21 days after the last application. The residues ranged from 0.12 to 0.46, 0.06 to 0.27 and 0.04 to 0.17 mg/kg after 7, 14 and 21 days PHI respectively.

Two additional studies were carried out in Switzerland (Kühne, 1993a,b), in one trial with one dip treatment in summer and one foliar application in the following spring, and in the other with a single dip in summer. Residues of 0.04 and <0.02 mg/kg respectively were detectable in the fruit the following season.

Four indoor and two outdoor residue trials (report nos. RVA 2108/80, 2109/80, 311-1986, 311-1987) were carried out in The Netherlands (1 or 2 treatments at 0.38-0.83 kg ai/ha) with maximum residues of 0.06 mg/kg (Anon., 1995b; Dornseiffen *et al*., 1989a,b).

The manufacturer also provided reports of a number of other residue trials carried out in

Canada, France, Germany, Italy, Switzerland, the UK and the USA (Leuthold, 1995) which had been submitted for the 1985 and 1987 Meetings. From one to five foliar applications were made with metalaxyl alone or mixed with mancozeb or folpet. Details of the new and the previously reported trials are shown Table 2. The underlined residues are from treatments according to GAP.

Table 2. Residues of metalaxyl in strawberries.

Country, year	Application				PHI, days	Residues, mg/kg		Report
	Form	No	kg ai/ha	kg ai/hl		Parent	Total*	
Outdoor								
Canada, 1980	WP	2	2.0 soil drench		44	0.02		RVA 2450/80
France, 1990	WP	2	0.7 foliar spray	0.007	26	0.26		60/90
Germany, 1981	WP	1	0.2 foliar spray before harvest		10	0.03		2091/82
1981	WP	3	0.2 foliar spray before harvest		10	0.08		2386/81
1982	WP	1	0.12[1] after harvest		289	<0.02		2033/81
					302	<0.02		
1982	WP	1	0.12[1] after harvest		309	<0.02		2051/82
					321	<0.02		
1983	WP	1	0.12[1] after harvest		251	<0.02		2052/82
					259	<0.02		
1983	WP	1	0.12[1] after harvest		233	<0.02		2290/82
					244	<0.02		
1983	WP	1	0.12[1] after harvest		222	<0.02		2291/82
					235	<0.02		
1983	WP	1	0.12[1] after harvest		218	<0.02		2292/82
					228	<0.02		
1983	WP	1	0.12[1] after harvest		229	<0.02		2293/82
					236	<0.02		
1984	WP	2	0.12[1] before flowering		75	0.09		2266/83
					84	0.09		
1984	WP	2	0.12[1] before flowering		91	0.02		2030/83
					96	0.02		
1984	WP	2	0.12[1] before flowering		79	0.16		2031/83
					87	0.11		
1984	WP	2	0.12[1] before flowering		78	0.1		2032/83
					88	0.06		
1987	WP	1	0.12[1] after harvest		239		0.02	RVA 2190/86
					247		<0.02	
1987	WP	1	0.12[1] after harvest		231		0.05	RVA 2191/86
					241		0.04	
1987	WP	1	0.12[1] after harvest		272		0.03	RVA 2192/86
					283		0.02	
1987	WP	1	0.12[1] after harvest		240		0.02	RVA 2193/86
					247		0.02	

Country, year	Application				PHI, days	Residues, mg/kg		Report
	Form	No	kg ai/ha	kg ai/hl		Parent	Total*	
Italy, 1980	GR	1	2.0 start of flowering		38	0.18		RVA 2129/80
1980	WP	1	2.0 full flowering		38	0.28		RVA 2130/80
Netherlands, 1980	WP	2	0.38 2 weeks after planting	0.02	86	<0.02		RVA 2108/80
1986	GR	1	0.38		28	0.04	<0.04	311-1986
					35	<0.04	<0.04	
					42	<0.04	<0.04	
1986	GR	1	0.38		42	0.06	0.06	311-1986
					49	0.06	0.04	
					56	0.04	0.05	
Spain,	WP	3	0.35 spraying before harvest	0.026	7	0.12		2057/93
1993				0.035	14	0.06		
				0.035	21	0.04		
1993	WP	3	0.35 spraying before harvest	0.058	7	0.28		2058/93
					14	0.18		
					21	0.09		
1993	WP	3	0.35 spraying before harvest	0.058	7	0.21		2059/93
					14	0.15		
					21	0.06		
1993	WP	3	0.35 spraying before harvest	0.082	7	0.21		2060/93
				0.073	14	0.15		
				0.073	21	0.06		
1993	WP	3	0.35 spraying before harvest	0.048	7	0.39		2061/93
					14	0.18		
					21	0.11		
1993	WP	3	0.35 spraying before harvest	0.046	7	0.46		2062/93
					14	0.27		
					21	0.17		
Switzerland, 1982	WP	1	0.06[2] 9 days after planting		286	<0.02		2034/81
1990	WP	1		0.05 dip				2116/90
		1	1.0 15-18 new leaves	0.1 foliar	52	0.04		
1990	WP	1		0.05 dip	317	<0.02		2116/90B
UK,	WP	1	0.12[2] soil drench after planting	0.05	71	0.09		RVA 2287/79
1979	WP	1	0.12[2] soil drench after planting	0.05	73	0.08		RVA 2288/79
1979	WP	1	0.12[2] soil drench after planting	0.05	82	<0.02		RVA 2289/79
USA, 1978	GR	5	2.2 young plants	0.24	200	<0.05		AG-A 6034
1982	EC	3	1.1	0.24	21	0.05, 0.08	0.09, 0.21	AG-A 6877

Country, year	Application				PHI, days	Residues, mg/kg		Report
	Form	No	kg ai/ha	kg ai/hl		Parent	Total*	
					28	0.07, 0.09	0.1, 0.11	
					35	<0.05 (2)	0.11 (2)	
1982	EC	3	1.1 foliar spray pre-bloom	0.12	32	0.26, 0.28	0.3, 0.35	AG-A 6979
					39	0.08, 0.21	0.15, 0.35	
1983	EC	3	1.1 foliar spray flowering	0.47	40		0.23, 0.24	AG-A 7402
					48		0.14 (2)	
					54		0.15, 0.17	
1985	GR	4	1.0		32		0.11, 0.12, 0.17, 0.34	AG-A 9225
	GR	1	1.0		34		0.12	
	GR	1	0.2[1]		71		<0.05(2), 0.08	
Indoor								
Netherlands, 1980	WP	1	0.83	0.02 dip	46	<0.02, 0.05		RVA 2109/80
		2		0.04 spray		0.06		
1987	GR	1	0.38		28	<0.05	<0.03	311-1987
					35	<0.05	<0.03	
					42	<0.05	<0.03	
	GR	1	0.38		56	<0.05	<0.05	
					63	<0.05	<0.05	
					70	<0.05	<0.05	

* sum of parent and all metabolites containing 2,6-dimethylaniline
[1] g/m, 0.12 corresponds to approx. 1.2 kg ai/ha
[2] g/plant, 0.12 corresponds to approx. 4.2-4.8 kg ai/ha

NATIONAL MAXIMUM RESIDUE LIMITS

The manufacturer reported only two new national MRLs for strawberries to the Meeting (Japan, USA). All national MRLs available for strawberries are shown below. For the other commodities see the 1992 JMPR evaluation.

National MRLs for strawberries.

Country	MRL in mg/kg
Austria	0.1
Belgium	0.1
France	0.5
Germany	0.1
Italy	0.5
Japan	0.5

Netherlands	0.1
Spain	0.5
USA	10

APPRAISAL

Metalaxyl was first evaluated in 1982 and has been reviewed several times since, most recently in 1992. At the 1994 CCPR the delegations of France, Germany and the EU questioned the basis for the maximum residue level for strawberry originally estimated by the 1985 JMPR and confirmed in 1992 (ALINORM 95/24 para 252). The Session was informed that the proposed MRL of 0.2 mg/kg would not cover all uses in the EU and the USA. The MRL was held at step 7B pending review by the 1995 JMPR.

Since metalaxyl has been proposed for periodic review, the Meeting considered only the MRL for strawberry. Other available information will be kept on file for consideration as part of the periodic review.

The Meeting received updated information on GAP, eight new residue reports and an overall assessment of the residue situation for strawberries by the manufacturer. Information on GAP for strawberries was provided by Canada and the UK. The Netherlands provided information on GAP, analytical methods and data on residues resulting from supervised trials.

The parent compound metalaxyl has been determined after extraction with dichloromethane, evaporation of the solvent and solution in hexane by GLC with nitrogen-specific detection (LOD 0.04 mg/kg). Metalaxyl and the metabolites containing the 2,6-dimethylaniline moiety were determined by GLC with nitrogen-specific detection (LOD 0.03 mg/kg) after extraction with dichloromethane, partitioning into water, acid hydrolysis of metalaxyl and the metabolites to 2,6-dimethylaniline, followed by bromination to 4-bromo-2,6-dimethylaniline. The LOD was 0.03 mg/kg.

The 1992 JMPR concluded that the available data did not support changing the MRL of 0.2 mg/kg. The present Meeting reviewed the new residue data in the context of earlier information.

The use of metalaxyl in strawberries is registered world-wide for foliar spray and broadcast or soil drench application. The Meeting noted the US tolerance for metalaxyl in strawberries (10 mg/kg) and was informed that although US GAP and data supporting the US tolerance were documented they had not been provided to the JMPR. This situation highlights the need for submission of all relevant data to the JMPR.

Only two outdoor residue studies approximating GAP were received. These were from The Netherlands (1 treatment of 0.38 kg ai/ha, 42-day PHI), with maximum residues of 0.06 mg/kg 42 days after treatment. The six new studies carried out in 1993 in Spain and the two from Switzerland were not in accord with current GAP, and the reports provided to previous JMPRs could not be used because the trials they described were not conducted according to current GAP.

In view of the known incompleteness of the submitted information on GAP and the lack of sufficient residue data to estimate a maximum residue level based on European GAP, the Meeting agreed to withdraw the previous recommendation of 0.2 mg/kg for strawberries.

RECOMMENDATIONS

The Meeting recommended the withdrawal of the previous recommendation for strawberry, as shown below.

Definition of the residue: metalaxyl

Commodity		Recommended limit, mg/kg		PHI on which based, days
CCN	Name	New	Previous	
	Strawberry	Withdrawn		

FURTHER WORK OR INFORMATION

Desirable

Residue data from supervised trials carried out in accordance with current use patterns on broccoli, cabbages and cauliflower (from 1992).

REFERENCES

Anon., 1994a. Information on GAP of Metalaxyl for the 1995 JMPR by Pesticides Safety Directorate United Kingdom, November 31, 1994. Unpublished.

Anon., 1994b. Information of the Netherlands on pesticides to be considered by the JMPR 1995 - Metalaxyl. Ministrie van Volksgezondheid, Welzijn en Sport Netherlands, September, 1994. Unpublished.

Anon., 1995a. Information on GAP and national MRLs of Metalaxyl for the 1995 JMPR by Agricultural and Veterinary Chemicals Policy Section of Department of Primary Industries and Energy, Australia, May 18, 1995. Unpublished.

Anon., 1995b. Information on GAP of Metalaxyl for the 1995 JMPR by Agriculture and Agri-Food Canada, Food Production and Inspection Branch, February 23, 1995. Unpublished.

Dornseiffen, J.W., den Ouden, J. and Verwaal, W. 1989a. Residuen van metalaxyl (en de metabolieten waaruit 2,6-dimethylaniline wordt afgesplitst) in aardbeien in de vollegrond (gekoelde teelt). KvW 286/CTM/PD 2502.300.311-1986. Food Inspection Service Amsterdam, The Netherlands, March 1989. Unpublished.

Dornseiffen, J.W., Enzler, K. and Verwaal, W. 1989b. Residuen van metalaxyl (en de metabolieten waaruit 2,6-dimethylaniline wordt afgesplitst) in aardbeien onder glas. KvW 287/CTM/PD 2502.300.311-1987. Food Inspection Service Amsterdam, The Netherlands, April 1989. Unpublished.

JMPR, 1992. Pesticides residues in food - 1992. Evaluations 1992, Part I - Residues. FAO Plant Production and Protection Paper 118, FAO, Rome 1993.

Kühne, R.O., 1993a. CGA 48988, RIDOMIL COMBI 50 WP, Strawberries, Switzerland, Ciba-Geigy Ltd. Basle, Rep. No. 2116/90, 07.10.1993. Unpublished.

Kühne, R.O., 1993b. CGA 48988, RIDOMIL COMBI 5 WP, Strawberries, Switzerland, Ciba-Geigy Ltd. Basle, Rep. No. 2116/90B, 07.10.1993. Unpublished.

Kühne, R.O., 1994a. CGA 48988, RIDOMIL 25 W, Strawberries, Spain, Ciba-Geigy Ltd. Basle, Rep. No. 2057/93, 07.07.1994. Unpublished.

Kühne, R.O., 1994b. CGA 48988, RIDOMIL 25 W, Strawberries, Spain, Ciba-Geigy Ltd. Basle, Rep. No. 2058/93, 07.07.1994. Unpublished.

Kühne, R.O., 1994c. CGA 48988, RIDOMIL 25 W, Strawberries, Spain, Ciba-Geigy Ltd. Basle, Rep. No. 2059/93, 07.07.1994. Unpublished.

Kühne, R.O., 1994d. CGA 48988, RIDOMIL 25 W, Strawberries, Spain, Ciba-Geigy Ltd. Basle, Rep. No. 2060/93, 07.07.1994. Unpublished.

Kühne, R.O., 1994e. CGA 48988, RIDOMIL 25 W, Strawberries, Spain, Ciba-Geigy Ltd. Basle, Rep. No. 2061/93, 07.07.1994. Unpublished.

Kühne, R.O., 1994f. CGA 48988, RIDOMIL 25 W, Strawberries, Spain, Ciba-Geigy Ltd. Basle, Rep. No. 2062/93, 07.07.1994. Unpublished.

Leuthold, U., 1995. Metalaxyl - Seventh Working Paper prepared by Ciba-Geigy Ltd., Basle February 1995. Unpublished.

METIRAM (186)

IDENTITY

Common name: metiram. No common name was accepted by ISO because the product appears to be a mixture rather than a complex (Tomlin, 1994).

Chemical name

IUPAC: zinc ammoniate ethylenebis(dithiocarbamate) - poly[ethylenebis(thiuram disulfide)]

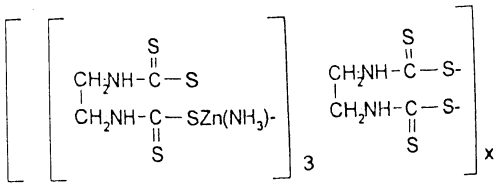
CA: metiram (composition not specified)

CAS No: [9006-42-2]

CIPAC No: 478

Synonyms: Polyram

Structural formula:



Molecular formula (monomer): $C_{16}H_{33}N_{11}S_{16}Zn_3$

Molecular weight: $(1088.6)_n$

Physical and chemical properties

Metiram pure active ingredient is inaccessible. In the manufacturing process ethylenediamine is reacted with carbon disulfide in ammonia solution to form an ammonium ethylenebis(dithiocarbamate). This intermediate is further reacted with zinc chloride and then with hydrogen peroxide to produce a polymeric precipitate. The gel-like filter cake (metiram TC, wet) consists of about 65% water, 30% metiram and 5% impurities which stabilize the structure of the polymer and optimise the fungicidal activity of the end product.

The filter cake is suspended in an aqueous solution of the formulation components and spray-dried.

The Meeting was provided with information on the composition of metiram TC (Ohnsorge, 1992).

Physical properties

Density, Polyram DF:	1.742 g/cm^3 (Gückel, 1992)
Bulk density, Polyram DF:	loose 533 g/l. tapped 571 g/l (Gückel, 1992)
Vapour pressure, metiram premix:	<0.01 mPa at 26.2°C (Gückel, 1988)
Water solubility, metiram technical:	approx 2 mg/l at 20°C (Keller and Pawliczek, 1985)
Octanol-water partition coefficient:	0.46-94 at pH 5. 0.19-2.5 at pH 7-9. (Keller, 1985a). Difficult to interpret because metiram is polymeric and a mixture.

Metiram in DMSO/water solution was degraded by UV light of wavelength 300 nm (Sarafin, 1992).

Formulations

Polyram Combi, WP. 70% metiram (formerly declared as 80% metiram complex, dry).

Polyram DF, WG. 70% metiram (formerly declared as 80% metiram complex, dry).

METABOLISM AND ENVIRONMENTAL FATE

Abbreviations of metabolites mentioned in metabolism studies

EDA	ethylenediamine
EU	ethyleneurea
ETU	ethylenethiourea
EBIS	ethylenebisisothiocyanate sulfide
ETT	ethylenethiourea-*N*-thiocarboxamide
EDTC	ethylenediisothiocyanate
JB	Jaffe's base 1-(2-imidazolin-2-yl)-2-imidazolidinethione
IMD	2-imidazoline

Animal metabolism

Information was made available to the Meeting on metabolism in lactating goats and laying hens.

Two lactating goats weighing 47 and 51 kg were dosed orally for 5 successive days by capsule with radiolabelled metiram, one with 1.49 g [*ethylenediamine*-^{14}C]metiram and the other with 1.6 g [*thiocarbamoyl*-^{14}C]metiram, equivalent to 1000 ppm metiram in the feed and 32 mg/kg bw (Holloway *et al*., 1986). The feed intake was a concentrate ration at 2.4% bw per day and 400 g straw per day. Milk was collected throughout, and the animals were slaughtered 5 hours after the final dose for tissue and organ collection.

The distribution of ^{14}C in the tissues, milk and excreta is shown in Table 1. The highest levels of metabolites were found in the thyroid, liver and kidneys.

Table 1. Distribution of radiolabel in the tissues, milk and excreta from 2 goats dosed orally for 5 days with [*ethylenediamine*-^{14}C]metiram or [*thiocarbamoyl*-^{14}C]metiram equivalent to 1000 ppm in the feed (Holloway *et al*., 1986).

Sample	thiocarbamoyl label		ethylenediamine label	
	^{14}C as % of total administered ^{14}C	^{14}C as metiram, mg/kg	^{14}C as % of total administered ^{14}C	^{14}C as metiram, mg/kg
Faeces	18		30	
Urine	11		22	
Milk, total	0.87	16	1.6	32
Muscle	0.97	20	1.3	29
Fat	0.04	3	0.06	4
Liver	0.93	83	1.3	118
Kidneys	0.14	84	0.17	97
Thyroid	0.01	128	0.02	346

Milk and tissues were examined for metabolites, but only EU and ETU could be positively identified. A major metabolite found in extracts of milk, kidneys, liver and muscle which could not be identified represented 40% and 66% of the ^{14}C in day-4 milk, corresponding to 14 and 15 mg/kg. The estimated levels in the tissues were kidneys 48 and 39 mg/kg, liver 25 and 22 mg/kg, and muscle 7 and 4 mg/kg. The residues of ETU and EU are shown in Table 2.

Table 2. Identified metabolites in milk and tissues from 2 goats dosed orally for 5 days with [*ethylenediamine*-^{14}C]metiram and [*thiocarbamoyl*-^{14}C]metiram equivalent to 1000 ppm in the feed (Holloway *et al*., 1986).

Sample	Metabolites, mg/kg as metiram			
	thiocarbamoyl label		ethylenediamine label	
	ETU	EU	ETU	EU
Milk, day 4	2	2	10	2
Kidneys	2	8	5	10
Liver	6	2	17	2
Muscle	10	10	17	4

Lactating goats (2 + 1 control, weighing 39, 44 and 41 kg) were dosed orally once daily for 5 days by gelatin capsule with 77 mg radiolabelled metiram ([^{14}C]ethylenediamine) equivalent to 50 ppm in the feed (Wu, 1989). The feed intake was 1.5 kg/animal/day. Milk and excreta were collected throughout and animals were slaughtered 8 hours after the final dose for tissue collection.

Most of the ^{14}C (75% of the dose) was excreted in the faeces. Excretion in the urine was also high; on the basis of the level of ^{14}C in the day 5 evening sample it was estimated that 54% of the dose was excreted in the urine. The total ^{14}C in the liver, kidneys, muscle and fat accounted for 1.5%, 0.17%, 0.03% and 0.02% of the administered dose respectively. The levels of ^{14}C in the milk rapidly reached a plateau within 1-2 days, and the total ^{14}C excreted in the milk (calculated from the level in the day 4 evening milk) accounted for approximately 0.77% of the dose.

Wu (1989) identified a number of the metabolites in the tissues and milk (Table 3). The total ^{14}C levels expressed as metiram were milk 0.61, liver 6.3 , kidneys 3.7, muscle 0.38 and fat 0.25 mg/kg.

Jaffe's base was a major metabolite in the milk, kidneys and muscle, while ETU constituted 9.4% of the residue in the fat. A considerable percentage of the ^{14}C in each tissue and in milk had been incorporated into natural products such as lactose, amino acids and lipids. The proposed metabolic pathways are shown in Figure 1.

Table 3. Distribution of metabolites and unknown compounds in milk and tissues from goats dosed orally once daily for 5 days by gelatin capsule with 77 mg radiolabelled metiram ([^{14}C]ethylenediamine) equivalent to 50 ppm in the feed (Wu, 1989).

Metabolite	Metabolite distribution as % of total ^{14}C in sample (mean from 2 goats)				
	Milk	Liver	Kidneys	Muscle	Fat
EBIS/ETT	0.40	0.87	0.47	3.1	-
JB	29	3.2	40	11	2.2
ETU	1.8	1.3	0.52	2.1	9.4
EU	5.8	2.9	4.5	9.1	1.8
EDA	2.2	5.1	2.8	3.0	4.5
Allantoin	-	3.5	3.4	5.0	-
Creatine	-	1.6	-	3.2	-
N-acetyl-EDA	0.43	-	0.53	0.63	-
Hydantoin	-	0.63	-	3.7	-
Creatinine	-	2.7	-	1.9	-
Glycine	3.7	15	6.3	5.3	2.9
N-formyl glycine	-	4.1	2.9	-	1.4
Lactose	17	-	-	-	-
Lipids	4.8	3.0	1.4	1.6	44
Amino acids	21	44	26	29	22
Unknowns	14	12	12	20	5.3

A group of 30 laying hens weighing 1.3-1.8 kg were dosed orally for 7 days by capsule with radiolabelled 6 mg metiram ([^{14}C]ethylenediamine), equivalent to 50 ppm metiram in the feed and 3.98 mg/kg bw (Merricks, 1988). The feed intake was 120 g/bird/day. Eggs were collected throughout, and birds were slaughtered 8 hours after the final dose for tissue and organ collection. Christman (1989) measured the levels of metiram and ETU in the tissues and eggs by chemical analysis. The results are shown in Table 4.

Table 4. Levels of metiram (as CS_2) and ETU in the tissues and eggs from hens dosed for 7 days with [^{14}C]ethylenediamine-labelled metiram equivalent to 50 ppm in the feed (Merricks 1988; Christman 1989). Chemical analysis.

Sample	Metiram as CS_2, mg/kg	ETU, mg/kg
Breast muscle	0.03 0.05	0.04 0.03
Thigh muscle	0.04 0.03	0.02 0.02
Fat	0.04 0.03	<0.01 <0.01
Liver	0.095 0.095	0.05 0.04
Egg white, day 6	0.02 0.02	0.05 0.07
Egg yolk, day 6	<0.02 <0.02	0.03 0.02

Wu (1990) identified the metabolites in the tissues and eggs (Table 5). The total ^{14}C levels expressed as metiram, mg/kg, were liver 3.7, kidneys 5.6, muscle 0.95, fat 0.24, skin 1.1, egg (day 5) 0.69, egg white (day 6) 0.61 and egg yolk (day 6) 1.0.

The major metabolite in all samples was EU. ETU was consistently present at 2-5% of the total ^{14}C. Lipids and proteins contained ^{14}C, showing that some of the metiram had been converted to natural products.

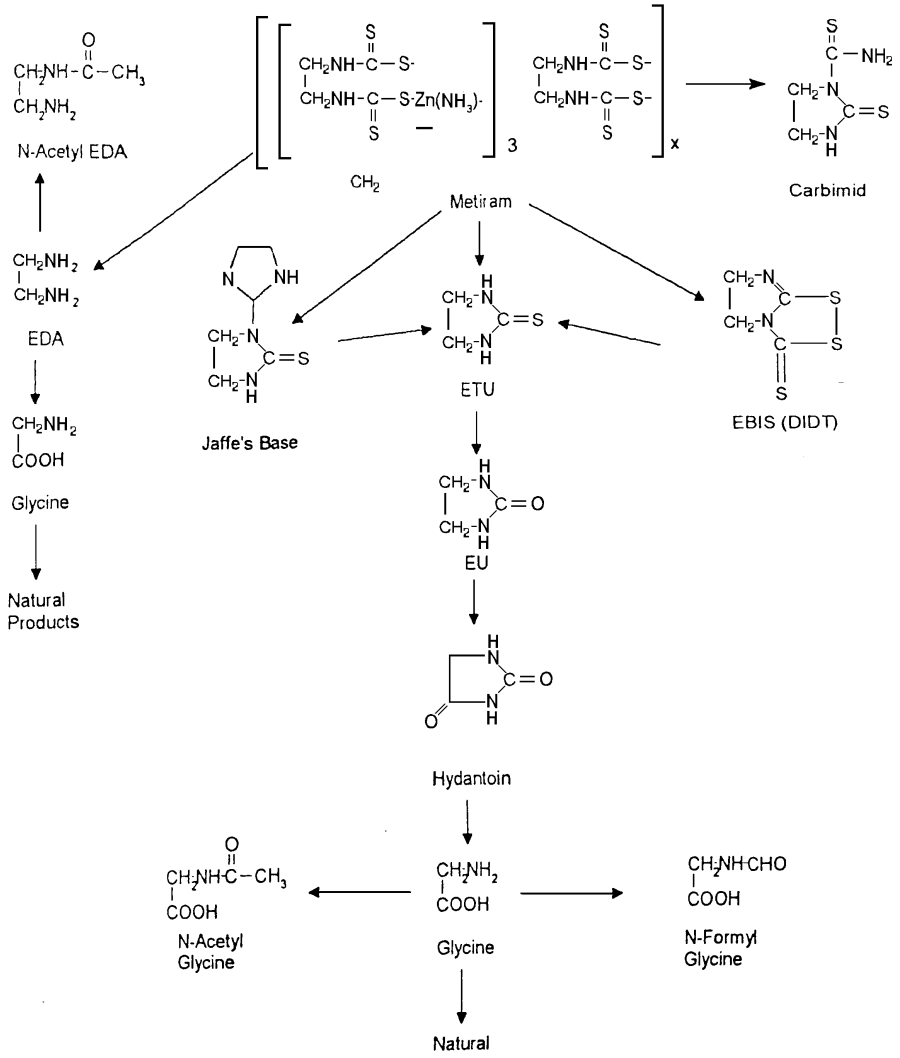
The metabolite pattern was reminiscent of those from mancozeb and maneb (1993 JMPR).

Table 5. Metabolites identified in the tissues and eggs from hens dosed for 7 days with [^{14}C]ethylenediamine-labelled metiram equivalent to 50 ppm in the feed (Merricks 1988; Wu 1990).

Metabolite	Metabolite expressed as % of total ^{14}C in sample (mean from 2 goats)						
	Muscle	Fat	Liver	Kidneys	Skin	Egg white	Egg yolk
EBIS/ETT	3.4	8.3	3.2	1.7	1.7	3.6	9.2
JB	6.4	3.2	4.5	2.8	7.3	1.7	11
ETU	3.6	4.9	2.7	1.8	3.3	2.8	2.5
EU	33	14	9.4	8.4	17	49	14
EDA	2.6	1.9	4.5	3.1		1.2	2.9
Allantoin	0.44	1.0	1.1	4.8			
Creatine		5.5	8.0		0.93		
N-acetyl-EDA	1.4			0.16	1.2		
Hydantoin	8.1				2.7		
Creatinine			2.1	3.5	1.0		
Glycine			5.8	5.4	0.78		

Christman (1989) showed that ETU and JB do not produce CS_2 during the CS_2-generating step in the determination of metiram. EBIS does produce CS_2.

Figure 1. Metabolic pathways of metiram in goats and laying hens.



Plant metabolism

Information was made available to the Meeting on metiram metabolism in apples and potatoes.

Apples, Cox's Orange variety, were treated 5 times with radiolabelled metiram ([^{14}C]ethylenediamine) at 1.4 kg ai/ha, and harvested 82 days after the final treatment (Bieber and Kröhn, 1986a). Residues of ^{14}C expressed as metiram were 0.93, 1.08 and 4.8 mg/kg in the flesh, core and peel respectively. Methanol extracted 56-75% of the total ^{14}C in each fraction but only 27-37% of the ^{14}C residues in each fraction

were soluble in acetone.

The acetone extracts from the flesh, core and peel were examined for the presence of ETU, EBIS, ETT, EDTC, EU and hydantoin, but they could not be detected. ETU levels would not have exceeded 0.005 mg/kg.

TLC analysis of the methanol extracts was not very successful, probably because of the content of sugar compounds. About 42% and 28% of the methanol-soluble ^{14}C from the peel corresponded on TLC to the metiram complex and oxalic acid respectively, and about 10% of that from the flesh to oxalic acid, but full identification was not possible. A further 10% corresponded to the metiram complex + glycine + *N*-acetylethylenediamine + *N*-formylglycine, but further identification was not possible.

Apples, Ana variety, were treated twice with radiolabelled metiram ([^{14}C]thiocarbonyl) at 2.4 kg ai/ha, and harvested 4 days after the final treatment (Bieber and Kröhn, 1986b). Residues of ^{14}C expressed as metiram were 3.0, 0.57, 20 and 45 mg/kg in the whole apple, flesh, peel and leaves respectively.

Aqueous methanol and dichloromethane extracted 46% of the total ^{14}C in the apples. Extracts of the fruit, peel and leaves were examined by TLC for likely metabolites, but ETU, EDTC, EBIS, ETT, EDA, EU and hydantoin could not be positively identified. However, analytical interferences from natural compounds in some cases prevented detection at low levels. Of the ^{14}C extracted from the peel and whole apples about 44% corresponded on TLC to the metiram complex, but identification could not be confirmed.

Potato plants, Grata-Mittelfrühe variety, were treated 4 times with radiolabelled metiram ([^{14}C]ethylenediamine) at 1.6 kg ai/ha, and tubers were harvested 28 days after the final treatment (Bieber and Kröhn, 1986c). Residues of ^{14}C expressed as metiram were 0.86 and 405 mg/kg in the tubers and tops respectively.

In the tubers 60% of the total ^{14}C was extractable with aqueous methanol. The extracts were examined for possible metabolites but ETU, EBIS, ETT and EDTC could not be detected. The level of ETU would not have exceeded 0.005 mg/kg. EU, hydantoin and EDA were possibly present at trace levels.

In the tops 34% of the ^{14}C was extractable into aqueous methanol: on TLC 60% of the extractable ^{14}C corresponded to the metiram complex and approximately 6% to ETU.

Potato plants, Holländer Erstlinge and Sieglind varieties, were treated twice with radiolabelled metiram ([^{14}C]thiocarbonyl) at 1.6 kg ai/ha, and tubers were harvested 29 days after the final treatment (Bieber and Kröhn, 1986d). Residues of ^{14}C expressed as metiram were 0.12 and 1146 mg/kg in the tubers and dry tops respectively.

In the tubers 54% of the total ^{14}C was extractable with aqueous methanol. The extracts were examined by TLC for possible metabolites but EU, ETU, EBIS, ETT, EDTC and hydantoin could not be detected. The level of ETU would not have exceeded 0.001 mg/kg. EDA was possibly present at trace levels.

In the tops 28% of the ^{14}C could be extracted into aqueous methanol. TLC analysis suggested the presence of ETU at a maximum of 1.8 mg/kg but confirmation was not possible. Low levels of EU, EDTC, EBIS, oxalic acid, glycine, *N*-acetylethylenediamine and *N*-formylglycine could not be excluded. Of the ^{14}C extracted from the tops about 67% corresponded on TLC to the metiram complex or a compound only slightly modified, but identification could not be confirmed.

Environmental fate in soil

Information was made available to the Meeting on the hydrolysis, photolysis, and degradation and mobility in soil of metiram, and on the hydrolysis and photolysis of ETU on soil.

Klein *et al.* (1985a) measured the aqueous hydrolysis rates of [*ethylene*-^{14}C]metiram and identified the hydrolysis products. Hydrolysis is accelerated at acid and alkaline pH. The rate of dissolution may be the rate-determining step.

pH	*Half-life (days) of suspended metiram*
3	*146*
5	*447*
7	*1075*
9	*174*

The reaction products were examined after 40 days hydrolysis of the suspended material in buffer solutions at 25°C and after 30 days hydrolysis of metiram pre-dissolved in DMSO, also in buffer solutions at 25°C. ETU was the main hydrolysis product in all the samples except the suspended material at pH 3 (Table 6).

Table 6. Products of hydrolysis of metiram at 25°C (Klein *et al*., 1985a).

Product	% of initial ^{14}C							
	Suspended				Pre-dissolved			
	pH 3	pH 5	pH 7	pH 9	pH 3	pH 5	pH 7	pH 9
EU	nd	nd	8.7	nd	nd	nd	4.3	13
ETU	25	95	87	67	69	95	91	87
Carbimid	nd	nd	nd	2.1	nd	nd	nd	nd
Hydantoin	3.8	5.4	nd	15	nd	nd	nd	nd
Unidentified polar	71	nd	4.2	13	28	4.8	5.2	nd

nd: not detected
Carbimid: 4,5-dihydro-1-thioformamido-1*H*-imidazole-2-thione

Klein *et al.* (1985b) showed that [*ethylene*-^{14}C]metiram was degraded by UV photolysis. The identified products are listed in Table 7. ETU is a major photolysis product.

Table 7. Products of photolysis of [^{14}C]metiram suspended in water or pre-dissolved in DMSO before being mixed with water (Klein *et al*., 1985b).

Product	% of initial ^{14}C		
	Metiram suspended in water, UV 5 days at 25°C	Metiram pre-dissolved in DMSO, then in water, UV 5 days at 25°C	Metiram pre-dissolved in DMSO, then in water, UV (xenon) 5 days at 35°C
ETU	55		72
EU		37	12
Hydantoin	18	16	

Klein *et al.* (1986b) studied the photolysis of [*ethylenediamine*-^{14}C]metiram applied at 8.5 mg/kg to a loamy sand (pH 5.7). The measured levels of the products of photolysis (or of metabolism by soil micro-organism) are shown in Table 8.

Table 8. Products of photolysis (or metabolism by soil micro-organisms) in a loamy soil following UV irradiation of soil treated with [*ethylenediamine*-^{14}C]metiram at 8.5 mg/kg (Klein *et al*., 1986b).

Product	^{14}C expressed as metiram, mg/kg							
	Days of irradiation							Non-irrad
	0	1	2	4	8	12	30	30
EU	1.1	0.81	1.0	0.94	0.68	1.0	0.59	0.29
ETU	0.38	0.22	0.2	0.30	0.19	0.47	0.19	nd
Hydantoin	nd	0.55	0.53	0.69	0.67	0.58	0.37	nd
Carbimid	1.5	0.53	0.4	0.42	0.13	0.29	nd	0.24

nd: not detectable

Keller and Huber (1985) showed that [*ethylenediamine*-^{14}C]metiram disappeared quickly from soil under aerobic conditions in laboratory incubation experiments. The dithiocarbamate remaining in the soil was measured by CS_2 evolution and spectrophotometry. The half-life was 25 hours in a loamy sand (pH 6.1) and 0.5 hours in a loam (pH 7.1). ETU and EBIS were identified and measured in methanol extracts of the soils. Conversion to these compounds occurred very rapidly and they, in turn, decreased within a few days (Table 9).

The mineralization rate of metiram was high with 42% of the ^{14}C in loamy sand and 43% in loam volatilized during 1 year of aerobic incubation.

To study anaerobic mineralization samples were incubated for 30 days aerobically followed by 30 days under anaerobic conditions. The mineralisation rate was slightly less than in the same soils under aerobic conditions for 60 days.

Table 9. Formation and decline of ETU and EBIS during aerobic incubation of [*ethylenediamine*-^{14}C]metiram for 60 days in a loamy sand and a loam (Keller and Huber, 1985).

Days	Loamy sand				Loam			
	ETU		EBIS		ETU		EBIS	
	mg/kg soil	% of initial ^{14}C	mg/kg soil	% of initial ^{14}C	mg/kg soil	% of initial ^{14}C	mg/kg soil	% of initial ^{14}C
0	0.22	2.2	4.3	43	0.30	3.0	5.6	57
1	0.23	2.3	1.7	17	0.31	3.3	2.7	28
2	0.05	0.5	0.80	8.3	0.46	4.9	1.1	12
4	0.05	0.5	0.50	5.4	1.2	13	0.52	5.5
7	-	-	0.45	5.1	1.0	11	0.28	3.0
14	-	-	0.23	2.9	-	-	0.19	2.0
21	-	-	0.14	1.9	0.12	1.4	0.06	0.7
30	-	-	0.17	2.4	0.06	0.7	0.22	2.7
60	0.03	0.5	0.03	0.5	-	-	0.09	1.3

Klein *et al.* (1986a) identified the products formed from [*ethylenediamine*-^{14}C]metiram incubated aerobically for 21 days in a loamy sand (pH 5.7) and their initial rates of disappearance.

Product	**Initial half-life, days**
ETU	1.6
EU	3.9
Carbimid	1.1
EBIS	1.7
Hydantoin	5.6

Rüdel (1990) studied the anaerobic degradation of [*ethylenediamine*-^{14}C]metiram in a loamy sand, pH 5.8. Metiram was applied to the soil at 8.6 mg/kg and incubated aerobically for 23 hours, and then anaerobically at 20°C. The initial aerobic period was chosen because the aerobic half-life for metiram was estimated to be 22.7 hours. The half-life of the parent metiram under anaerobic conditions was 14.5 days, and 16% of the initial ^{14}C was mineralised in 60 days. After 60 days the identified products were ethanolamine, glycine, ETU, carbimid, EBIS, hydantoin and EU.

Spare (1988a) investigated the leaching characteristics of [*ethylenediamine*-^{14}C]metiram in four soil types: a sand (pH 6.5), a sandy loam (pH 6.5), a silt loam (pH 5.9) and a clay (pH 7.5). Samples of soils treated at 10 mg/kg with [^{14}C]metiram were placed on top of soil columns (30 cm) and eluted slowly (3-12 days) with a volume of deionised water equivalent to a 51 cm length of the column. The distribution of ^{14}C in the soil columns and leachates showed that leaching occurred most readily in the sand, and very little in the clay. Substantial amounts of the ^{14}C still remained at the top of the column, with 15%, 35%, 80% and 70% remaining in the top 2.5 cm of the sand, sandy loam, clay and silt loam respectively. ETU was not detectable in methanol extracts of the soil columns.

	^{14}C as % of initial dose			
	sand	sandy loam	clay	silt loam
soil column	40%	62%	90%	88%
leachate	57%	28%	2%	13%

Sections of the soil columns, 0-2.5 cm, 2.5-5 cm, 5-7.5 cm and 7.5-10 cm, were analysed for dithiocarbamates by a CS_2 evolution method, but none were detected with an LOD, as CS_2, of 0.03 mg/kg (Larese, 1988e).

Spare (1988b) identified products of [^{14}C]metiram in the leachates from the soil columns (Table 10). EU, hydantoin and IMD were the major compounds. ETU accounted for approximately 4% of the ^{14}C in each of the leachates.

Table 10. Labelled compounds identified by TLC in leachates from soil columns to which [^{14}C]metiram had been applied (Spare 1988b).

Compound	Compound as % of applied ^{14}C		
	sand	sandy loam	silt loam
ETU	2.4	1.3	0.5
IMD	14	4.0	4.1
EU	18	11	2.8
Hydantoin	12	9.1	2.2
Glycine	2.5	2.4	0.3
Oxalic acid	1.8	0.1	0.7

Carpenter (1987a) showed that the half-life of ETU on a silty loam exposed to a xenon arc UV lamp was 1.3 days, which was less than its half-life of 2.5 days on the same soil in the dark. TLC

analysis of solvent extracts of the soil showed the presence of ETU, EU, 2-imidazoline and three unidentified compounds. The degradation products in the extracts of the exposed soil and the dark controls were the same. The conclusion was that photodegradation contributes little to the total degradation of ETU.

ETU was shown to be stable to hydrolysis at 25°C in the pH range 5 to 9 (Carpenter, 1987b). The degradation over 30 days in aqueous buffers at pH 5, 7 and 9 was so slight that no estimate of half-life was possible.

METHODS OF RESIDUE ANALYSIS

Analytical methods

The analytical methods for metiram rely on acid hydrolysis to release CS_2, which is then measured colorimetrically or by gas chromatography. The methods are the same as those for the other ethylenebis(dithiocarbamates), mancozeb and maneb.

Metiram residues in the sample generate CS_2 when it is treated with stannous chloride and hydrochloric acid (BASF, 1978). The CS_2 is distilled into methanolic potassium hydroxide and forms a dithiocarbonate which is measured by UV spectrophotometry at 302 nm. Limits of determination are in the range 0.02-0.2 mg/kg depending on the type of sample. Alternatively, the dithiocarbonate is derivatized to produce methyl *N*,*N*-dipropyldithiocarbamate and determined by GLC. The limit of determination is about 0.02 mg/kg.

Tilting (1985b) used a similar method for the residue analysis of animal commodities, but collected the evolved CS_2 in pure methanol and determined it by GLC with a sulfur-selective FPD. Recoveries varied from 50 to 100%. Limits of determination were in the range 0.02-0.4 mg/kg (as CS_2). Tilting (1985a) also used the UV spectrophotometric method for the analysis of animal commodities but interferences were more prevalent than in plant samples.

The liberated CS_2 may also be measured colorimetrically (Thier and Zeumer, 1987b). A cupric acetate reagent forms yellow-coloured copper dithiocarbamate complexes which absorb light at 435 nm. Sample blanks occurred with a few crops: rape seed, rutabaga, cauliflower and Savoy cabbage.

In the method of the Dutch manual of analytical methods (Ministry of Welfare, Health and Cultural Affairs, 1988) metiram is converted to CS_2 by treatment with hydrochloric acid in the presence of stannous chloride. The CS_2 in the head-space is determined by GLC with either an ECD or an FPD in the sulfur mode.

Ethylenebisdithiocarbamates and propylenebisdithiocarbamates can be separated by gel permeation chromatography (Thier and Zeumer, 1987c). Because these residues are present only on the surface and not within harvested crops they are removed from the plant material with an aqueous solution of ethylenedinitrilotetra-acetic acid (tetrasodium salt). The disodium ethylenebisdithiocarbamates and propylenebisdithiocarbamates are separated on Sephadex LH-20 and determined by their UV absorbance at 285 nm. Routine limits of determination range from 0.05 to 0.5 mg/kg.

Methods for the residue analysis of ethylenethiourea were reviewed in the 1993 monograph on mancozeb. The GLC methods for ETU residues in plant and animal commodities which were used in the supervised trials were made available to the Meeting (BASF, 1980; Keller, 1985b). The method for ETU in plant materials has been published (Thier and Zeumer, 1987a).

ETU was determined in grapes and wine by GLC after derivatization to *S*-benzyl-ETU (Chovancová *et al.*, 1985). Care was taken to minimise conversion of EBDCs to ETU during derivatization.

Zafiriou (1985) analysed apple and peach juices for ETU residues by a GLC method which measured ETU directly without derivatization. Good recoveries were achieved down to 0.02 mg/kg.

Stability of pesticide residues in stored analytical samples

Information was made available on the storage stability of metiram and ETU on apples, wet and dry apple pomace, apple juice, sauce, baby food, tomatoes, potatoes and sugar beets. Studies of the frozen storage stability of ETU in a number of commodities were included in the 1993 monograph on mancozeb.

Metiram was sprayed on apple orchards in New York and North Carolina and samples were collected 28 days after the final application (Bookbinder, 1988). Metiram was applied to each orchard 13 times (7×7.2 kg ai/ha + 6×5.4 kg ai/ha) using 3700 litres of spray per hectare. Apple samples were frozen after collection, shipped frozen to the analytical laboratory, and stored frozen (-20°C) until preparation and analysis. The results are shown in Table 11.

Metiram residues were stable in the frozen apples, with approximately 20% decline in 12 months. ETU residues were formed during storage and accumulated at the longer intervals demonstrating that ETU residues are stable in frozen whole apples at -20°C.

Table 11. Residues of metiram (as metiram) and ETU in field-treated apples from North Carolina and New York stored at -20°C (Bookbinder, 1988; Larese, 1989b). Apples were harvested 28 days after the last of 13 applications (7×7.2 kg ai/ha + 6×5.4 kg ai/ha).

Storage interval	Residues, mg/kg			
	NY apples		NC apples	
	Metiram	ETU	Metiram	ETU
0 day	3.8 3.7		5.8 6.0	
2 weeks	3.7 3.7		5.9 5.8	
1 month			5.8 5.7	0.11 0.13
3 months			5.2 5.1	0.26 0.24
6 months			5.05 4.95	0.16 0.16
12 months			4.79 4.69	0.24 0.32

Larese (1988a, 1989a) reported on the storage stability of metiram and ETU in spiked samples of diced apples frozen and stored at -20°C. The results are shown in Table 12. Metiram was stable for 12 months but ETU disappeared within weeks.

Table 12. Residues of metiram (as metiram) and ETU in spiked samples of apples stored at -20°C (Larese, 1988a,1989a).

Storage interval	Residues, mg/kg			
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg	
	Metiram	ETU	ETU, run 1	ETU, run 2
0 day	1.90 1.96	<0.01 <0.01	0.20 0.20	0.17 0.21
2 weeks	1.87 1.89	0.01 <0.01	0.01 0.01	0.17 0.18
1 month	1.91 1.90	0.01 <0.01	<0.01 <0.01	0.03 0.03
3 months	1.68 1.64	0.01 <0.01		0.02 0.03
6 months	1.65 1.67	<0.01 0.01		<0.01 <0.01
12 months	1.54 1.56	<0.01 0.01		<0.01 <0.01

Larese (1989c) fortified frozen apple commodities with metiram (2.0 mg/kg) or ETU (0.20 mg/kg) and measured the stability of the residues at -20°C during storage intervals up to 12 months. The results are shown in Table 13. Metiram was shown to be stable in the commodities studied: apple sauce, apple juice and apple baby food. There was little conversion of metiram to ETU. ETU itself in these substrates stable during storage.

Anomalous results for apple juice at the 1- and 3-months intervals were further investigated. A small change in the procedure had been inadvertently introduced which resulted in the presence of metiram during the derivatization of ETU, and some conversion of metiram to ETU was occurring. Later samples were analysed by the corrected procedure.

Table 13. Residues of metiram (as metiram) and ETU in spiked samples of frozen apple sauce, fresh apple juice, cooked apple juice and apple baby food stored at -20°C (Larese, 1989c).

Storage interval	Residues, mg/kg		
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg
	Metiram	ETU	ETU
APPLE SAUCE			
0 day	1.96 1.93	<0.01 <0.01	0.17 0.17
2 weeks	1.83 1.86	<0.01 <0.01	0.14 0.16
1 month	1.89 1.91	<0.01 <0.01	0.16 0.12
3 months	1.83 1.90	<0.01 <0.01	0.14 0.17
6 months	1.88 1.84	0.01 <0.01	0.11 0.12
12 months	1.70 1.80	<0.01 <0.01	0.11 0.10
FRESH APPLE JUICE			
0 day	1.93 1.92	0.05 0.07	0.13 0.14
2 weeks	1.87 1.89	0.06 0.07	0.14 0.16
1 month	1.85 1.83	0.18 0.16	0.16 0.16
3 months	1.81 1.80	0.34 0.42	0.20 0.19
4.5 months		0.03 0.03	
6 months	1.82 1.76	0.03 0.02	0.15 0.12
12 months	1.57 1.65	0.03 0.03	0.13 0.14
COOKED APPLE JUICE			
0 day	1.84 1.85	0.03 0.03	0.15 0.15
2 weeks	1.83 1.80	0.05 0.06	0.12 0.13
1 month	1.82 1.79	0.13 0.14	0.13 0.13
3 months	1.85 1.87	0.32 0.32	0.20 0.20
4.5 months		0.04 0.05	
6 months	1.85 1.84	0.01 0.02	0.12 0.13
12 months	1.82 1.84	<0.01 <0.01	0.12 0.14
APPLE BABY FOOD			
0 day	1.91 1.92	0.03 0.04	0.22 0.23
2 weeks	1.92 1.89	0.04 0.04	0.16 0.18
1 month	1.95 1.96	0.03 0.04	0.22 0.20
3 months	1.95 1.93	0.07 0.06	0.21 0.19
6 months	1.90 1.84	0.06 0.06	0.22 0.19
12 months	1.88 1.81	0.03 0.03	0.18 0.18

Data on the frozen storage stability of metiram and ETU in apple pomace are summarized in Table 14 (Larese, 1989d). The frozen commodities were fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 12 months at -20°C. Metiram was adequately stable under the conditions, and produced little ETU. ETU disappeared very quickly from wet pomace, but was stable in dry pomace.

Table 14. Residues of metiram (as metiram) and ETU in spiked samples of frozen wet and dry apple pomace stored at -20°C (Larese, 1989d).

Storage interval	Residues, mg/kg		
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg
	Metiram	ETU	ETU
WET POMACE			
0 day	1.86 1.87	<0.01 <0.01	0.18 0.16
2 weeks	1.89 1.89	<0.01 <0.01	<0.01 <0.01
1 month	1.81 1.86		
3 months	1.80 1.82	<0.01 <0.01	<0.01 <0.01
6 months	1.76 1.74	0.01 <0.01	<0.01 <0.01
12 months	1.60 1.58	<0.01 <0.01	<0.01 <0.01
DRY POMACE			
0 day	1.71 1.70	0.01 0.01	0.18 0.16
2 weeks	1.82 1.77	0.01 0.01	0.17 0.18
1 month	1.75 1.76	0.04 0.02	0.14 0.14
3 months	1.77 1.80	0.01 0.01	0.15 0.09
6 months	1.62 1.55	<0.02 <0.02	0.11 0.10
12 months	1.46 1.39	<0.02 <0.02	0.12 0.11

Data on the frozen storage stability of metiram and ETU in frozen diced tomatoes are shown in Table 15 (Larese 1988b, 1989e). The frozen tomatoes were fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 12 months at -20°C. Metiram was stable under the conditions, and produced very little ETU. ETU residues were reasonably stable for 12 months.

Table 15. Residues of metiram (as metiram) and ETU in spiked samples of frozen diced tomatoes stored at -20°C (Larese 1988b, 1989e).

Storage interval	Residues, mg/kg		
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg
	Metiram	ETU	ETU
0 day	1.89 1.87	<0.01 <0.01	0.20 0.20
2 weeks	1.94 1.95	0.01 0.03	0.17 0.17
1 month	1.91 1.90	0.01 0.01	0.15 0.12
3 months	1.80 1.83	0.01 0.01	0.14 0.15
6 months	1.76 1.72	0.01 0.01	0.16 0.16
12 months	1.73 1.67	0.02 0.02	0.12 0.12

The results of frozen storage stability studies on metiram and ETU in frozen diced potatoes are

shown in Table 16 (Larese 1988c, 1989f). The frozen potatoes were fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 1 or 3 months at -20°C. Metiram was stable under the conditions, and very little ETU was produced. ETU disappeared very quickly with 70-80% loss in 2 weeks. Because of the early disappearance of ETU the first ETU run was abandoned after 1 month and the analyses repeated in run 2.

Table 16. Residues of metiram (as metiram) and ETU in spiked samples of frozen diced raw potatoes stored at -20°C (Larese, 1988c, 1989f)

Storage interval	Residues, mg/kg			
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg	
	Metiram	ETU (run 2)	ETU, run 1	ETU, run 2
0 day	1.92 1.96	0.01 0.01 (0.02 0.02)	0.19 0.20	0.18 0.18
2 weeks	1.92 1.89	0.02 0.02 (0.03 0.02)	0.06 0.02	0.07 0.05
1 month	1.89 1.91	0.02 0.09 (0.03 0.03)	0.03 0.02	0.07 0.06
3 months	1.77 1.75	(0.02 0.02)		0.05 0.05
6 months	1.67 1.69	(0.01 0.01)		0.01 <0.01
12 months	1.60 1.54	(0.02 0.01)		0.01 0.01

Data on the frozen storage stability of metiram and ETU in frozen diced sugar beet are shown in Table 17 (Larese 1988d, 1989g). The frozen beet was fortified with either metiram at 2.0 mg/kg or ETU at 0.20 mg/kg and stored for 1 or 3 months at -20°C. Metiram was stable under the conditions. ETU disappeared quickly with about 60% loss in one month. The first ETU run was therefore again abandoned after 1 month and the analyses repeated in run 2.

Table 17. Residues of metiram (as metiram) and ETU in spiked samples of frozen diced sugar beet stored at -20°C (Larese, 1988d, 1989g)

Storage interval	Residues, mg/kg			
	Metiram added at 2.0 mg/kg		ETU added at 0.20 mg/kg	
	Metiram	ETU (run 2)	ETU, run 1	ETU, run 2
0 day	1.86 1.88	0.02 0.02 (0.02 0.02)	0.21 0.20	0.18 0.18
2 weeks	1.92 1.92	0.05 0.04 (<0.01 <0.01)	0.09 0.07	0.11 0.10
1 month	1.89 1.90	0.04 0.03 (0.02 0.01)	0.06 0.06	0.08 0.08
3 months	1.86 1.85	(0.01 0.03)		0.03 0.04
6 months	1.74 1.74	(0.02 0.01)		0.03 0.05
12 months	1.62 1.49	(<0.01 <0.01)		0.05 0.02

Residue definition

Metiram is a dithiocarbamate and will be included in the definition of dithiocarbamate residues. Supervised trials data have been generated using methods which measure the CS_2 evolved during acid digestion. In the regulatory analytical methods for dithiocarbamates metiram residues will behave in the same way as other dithiocarbamate residues.

An analyst using an enforcement method will measure the total evolved CS_2 produced by acid digestion of a sample, which will not indicate its source.

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The Meeting proposed a revised dithiocarbamate residue definition:

The MRLs refer to total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg.

USE PATTERN

Metiram is a non-systemic fungicide with a very broad spectrum of activity. It is effective against downy mildews (*Peronospora sp.*), rust fungi (*Uromyces sp.*, *Puccinia sp.*) and a number of leaf spot fungi (*Septoria sp.*, *Venturia sp.*). Metiram is used on cereals, fruits, vegetables, tobacco and ornamentals.

Metiram inhibits the sporulation of fungi by specific binding to SH-containing enzyme systems within the fungi. Resistance to metiram is not expected to develop, because of this multi-site inhibition activity. Resistance has not developed in more than 30 years of use.

Metiram formulations are registered in many countries. The registered uses are shown in Table 18.

Table 18. Registered uses of metiram.

Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Apple	Argentina	WG	spray		0.12-0.16	4	20
Apple	Argentina	WP	spray			1-4	20
Apple	Australia	WP WG	spray		0.12-0.16		21
Apple	Belgium	WP	spray				10
Apple	Belgium	WP	mist	1.8			21
Apple	Bolivia	WG	spray		0.15-0.20	6-10	
Apple	Bulgaria	WP					14
Apple	Canada	WG	spray	4.8			45
Apple	Chile	WG	spray			7-10	14
Apple	Croatia	WP					28
Apple	Denmark	WP	mist	1.75			28
Apple	Greece	WP WG	spray				
Apple	Hungary	WG		1.8	0.58		30
Apple	Indonesia	WP					
Apple	Ireland	WG	spray	1.8	0.33		
Apple	Italy	WP WG	spray		0.10-0.14		28
Apple	Luxembourg	WP	spray	0.019	0.0019		14
Apple	Macedonia	WP					
Apple	Morocco	WP	spray				14
Apple	Mozambique	WP					
Apple	Netherlands	WG	mist				28
Apple	Netherlands	WP	mist			8	28
Apple	Netherlands	WP	spray	1.8	0.16	7-10	28
Apple	New Zealand	WP WG	spray		0.07-0.11	10	14
Apple	Paraguay	WP	spray				
Apple	Poland	WP					35
Apple	Portugal	WP WG	spray		0.14		7
Apple	Rumania	WP WG					
Apple	Sth Africa	WP	LV spray	4.6	0.40-0.52	9	21
Apple	Sth Africa	WP	spray	5.6	0.12-0.16	9	14
Apple	Switzerland	WP	spray	1.9			21
Apple	Turkey	WP	spray	1.5	0.15	2-3	28
Apple	Turkey	WG	spray	1.6	0.16	1-2	21
Apple	UK	WP	mist	0.038			14
Apple	USA	WP WG	spray	5.4	2.9	4	pre-flower
Apple	USA	WP WG	spray	2.7	1.5	7	77
Apple	Yugoslavia	WP					28
Apple	Zimbabwe	WP					14

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Apricot	Sth Africa	WP	spray		0.12-0.16		14
Asparagus	Australia	WP WG	spray	2.8	0.16-0.26		7
Asparagus	Belgium	WG	spray	2.5			28
Asparagus	Canada	WG	spray	2.6		4	after spears removal
Asparagus	Costa Rica	WP	spray	1.6			
Asparagus	Costa Rica	WG	spray	1.6	0.12-0.16		7
Asparagus	Dominican	WG	spray	1.4			7
Asparagus	Germany	WG	spray	0.84		1-4	
Asparagus	Germany	WP	spray	0.96		4	2
Asparagus	Greece	WP WG	spray	1.6			
Asparagus	Luxembourg	WG	spray	2.5			28
Asparagus	Paraguay	WP	spray			2	
Banana	Ecuador	WP	spray	0.72	0.36		14
Barley	Ireland	WG	spray	1.4	0.56	2	28
Barley	UK	WP	spray	1.4	0.56	1-2	28
Bean	Argentina	WG	spray		0.16	1-4	10
Bean	Argentina	WP	spray	1.6		3	10
Bean	Australia	WG	spray	2.8	0.26		7
Bean	Belgium	WG	spray		0.32		28
Bean	Bolivia	WG	spray	1.4	0.47	3-6	
Bean	Bulgaria	WP	seed treat				
Bean	Costa Rica	WG	spray	1.6			7
Bean	Costa Rica	WP	spray	1.4			
Bean	Dominican	WG	spray	1.4			7
Bean	Ecuador	WP	spray	1.6	0.16	3	7
Bean, Climbing	Germany	WP	dry dressing			1	2
Bean	Greece	WP WG	spray	1.4			
Bean	Luxembourg	WG	spray				28
Bean	Malaysia	WP WG					14
Bean	Paraguay	WP	spray			2	
Bean	Peru	WG		0.80			7
Bean	Spain	WP WG	spray		0.12-0.16		15
Bean	Sth Africa	WP	spray	1.6	0.16		3
Bean	Zimbabwe	WP					3
Bean, Broad	Peru	WP	spray			3-6	7
Bean, Dwarf	Germany	WP	dry dressing			1	2
Bean, Dwarf	Germany	WP	spray	0.96		2	7
Beet	Bulgaria	WP	seed treat				
Blueberry	Greece	WP WG	spray				
Blueberry	Paraguay	WP	spray				
Broccoli	Australia	WG	spray	2.8			7
Broccoli	Costa Rica	WG	spray	1.2	0.32-0.50		7
Broccoli	Mozambique	WP					
Brussels sprouts	Australia	WG	spray	2.8			7
Cabbage	Australia	WG	spray	2.8			7
Cabbage	Bolivia	WG	spray		0.20	5-15	
Cabbage	Costa Rica	WG	spray	1.2			7
Cabbage	Costa Rica	WP	spray	1.4			
Cabbage	Dominican	WG	spray	1.4			7
Cabbage	Germany	WP	dry dressing			1	2
Cabbage	Greece	WP WG	spray	1.4			
Cabbage	Ireland	WG	spray	1.4	0.64		
Cabbage	Malaysia	WP WG					14
Cabbage	Paraguay	WP	spray	0.005		2	
Cabbage	Poland	WP					
Cacao	Costa Rica	WP	spray				

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Cacao	Dominican	WG	spray				7
Cacao	Indonesia	WP	spray	0.64	0.16		
Carrot	Australia	WP WG	spray	1.8	0.16		7
Carrot	Bolivia	WG	spray	1.4	0.47	5-10	
Carrot	Canada	WG	spray	1.8			5
Carrot	Costa Rica	WP	spray	1.6			
Carrot	Dominican	WG	spray				7
Carrot	Greece	WP WG	spray	1.4			
Carrot	Mozambique	WP					
Carrot	Paraguay	WP	spray			2	
Cauliflower	Australia	WG	spray	2.8			7
Cauliflower	Mozambique	WP					
Celery	Argentina	WP					3
Celery	Australia	WP WG	spray	1.8	0.16		2
Celery	Belgium	WG	spray		0.16		28
Celery	Canada	WG	spray	2.6			14
Celery	Canada	DP	spray	3.5			14
Celery	Costa Rica	WP WG	spray	1.6			7
Celery	Dominican	WG	spray	1.4			7
Celery	Germany	WP	spray	1.4		4	28
Celery	Greece	WP WG	spray	1.4			
Celery	Luxembourg	WG	spray				28
Celery	Malaysia	WP WG					14
Celery	Paraguay	WP	spray			2	
Celery	Peru	WP	spray			3-6	7
Celery	Peru	WG		0.80		2-3	7
Celery	Poland	WP		1.6			
Celery	Spain	WP	spray		0.12-0.16		15
Cereals	Belgium	WG	spray	1.4			28
Cereals	Hungary	WG		1.4			52
Cereals	Italy	WP WG	spray	2.1			28
Cereals	Italy	WP	seed dressing				28
Cereals	Luxembourg	WG	spray	1.4			28
Cherry	Costa Rica	WP	spray				
Cherry	Greece	WP WG	spray				
Cherry	Paraguay	WP	spray			2-4	
Cherry	Switzerland	WP WG	spray				21
Citrus	Argentina	WG	spray		0.12-0.16		10
Citrus	Argentina	WP	spray			3	10
Citrus	Costa Rica	WG		1.6			7
Citrus	Cyprus	WP WG			0.15-0.20		7
Citrus	Dominican	WG	spray				7
Citrus	Greece	WP WG	spray				
Citrus	Jordan	WP	spray	1.2	0.2	1-3	
Citrus	Mozambique	WP					
Citrus	Paraguay	WP	spray				
Cotton	Costa Rica	WP	spray				
Cotton	Greece	WP WG	seed dressing				
Cotton	Paraguay	WP	spray				
Cotton	Peru	WG		0.80		1	7
Cotton	Peru	WP	spray			3-5	7
Cranberry	Costa Rica	WP	spray				
Cucumber	Australia	WG					2
Cucumber	Bolivia	WG	spray	1.4	0.23	3-15	
Cucumber	Costa Rica	WG		1.6	1.6		7
Cucumber	Costa Rica	WP	spray	1.4			
Cucumber	Dominican	WG	spray	1.4			7

Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Cucumber	Israel	WG		2.0			5
Cucumber	Malaysia	WP WG					14
Cucumber	Mozambique	WP					
Cucumber	Paraguay	WP	spray			2	
Cucumber	Rumania	WP WG					
Cucumber	Spain	WP	spray		0.12-0.16		15
Cucumber	Zimbabwe	WP					14
Cucurbits	Mozambique	WP					
Cucurbits	Pakistan	WP					
Cucurbits	Spain	WP	spray		0.12-0.16		15
Currants Black, Red	Poland	WP					
Currant, Red	Costa Rica	WP	spray				
Currant, Red	Germany	WP	spray		0.12	4	35
Currant, Red	Greece	WP WG	spray				
Field crops	Saudi Arabia	WP	spray	0.80	0.20	1-3	
Fruit	Algeria	WP					
Fruit	Angola	WP	spray	0.50	0.20		
Fruit	Argentina	WP	spray				
Fruit	Peru	WP		2.2			
Fruit	Saudi Arabia	WP	spray	0.80	0.20	1-3	
Fruit	Tunisia	WP	spray			3-4	
Fruits, tropical	Costa Rica	WP	spray				
Garlic	Dominican	WG	spray	1.4			7
Garlic	Israel	WG		2.0			
Gooseberry	Costa Rica	WP	spray				
Gooseberry	Greece	WP WG	spray				
Gooseberry	Paraguay	WP	spray				
Gooseberry	Poland	WP					
Grape	Argentina	WG	spray	1.8	0.16	3	10
Grape	Argentina	WP	spray			3	10
Grape	Australia	WP WG	spray		0.12-0.16		14
Grape	Austria	WG	spray				14
Grape	Austria	WP	spray			6-8	14, 42
Grape	Bolivia	WG	spray		0.15-0.20	3-6	
Grape	Bulgaria	WP					14
Grape	Canada	WG	spray	1.6	0.16	1-3	45
Grape	Canada	DP	spray	4.7		1-3	45
Grape	Costa Rica	WP	spray				
Grape	Croatia	WP					
Grape	Czech	WP					21
Grape	France	WP	spray	2.5			
Grape	France	WG	spray	2.8			
Grape	Germany	WP	spray			1-8	56
Grape	Germany	WG	spray		0.16	1-6	56
Grape	Greece	WP WG	spray				
Grape	Hungary	WG		1.8	0.58		21
Grape	Italy	WP	spray	1.5	0.10-0.28	3	28
Grape	Italy	WG	spray				28
Grape	Jordan	WP	spray	1.2	0.2	1-3	
Grape	Macedonia	WP					
Grape	Mozambique	WP					
Grape	New Zealand	WG	spray		0.14	12	14
Grape	Paraguay	WP	spray			3	
Grape	Portugal	WP WG	spray		0.14-0.28		7
Grape	Rumania	WP WG					
Grape	Spain	WP WG	spray	2.4	0.12-0.16	1-6	15
Grape	Switzerland	WP WG	spray				21

Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Grape	Tunisia	WP	spray	0.74	0.21	4	
Grape	Tunisia	WP	spray	2.8	0.28	3-4	
Grape	Turkey	WG	spray	0.64	0.16	2-3	56
Grape	Uruguay	WP	spray	2.4	0.16	4-6	25
Grape	Yugoslavia	WP					
Grape	Zimbabwe	WP				6-9	14
Grapes, table	Sth Africa	WP	spray	2.4	0.16		not after pea size
Grapes, wine	Sth Africa	WP	spray	2.4	0.16		14
Hops	Belgium	WG	mist		0.16-0.20		42
Hops	Czech	WP					
Hops	Germany	WP WG	spray		0.16	1-12	35
Hops	Hungary	WG		1.8	0.44		14
Hops	Ireland	WG	spray	1.4	0.14		
Hops	Luxembourg	WG	mist				42
Hops	Morocco	WP	spray				14
Hops	Poland	WP					
Hops	Switzerland	WG	spray			12	35
Hops	UK	WG	mist	1.6			
Hops	UK	WP	mist	1.4	0.56		
Hops	UK	WG	spray	1.6			
Leaf and stem vegetables	Australia	WP	spray	1.8	0.16		7
Legumes	Australia	WP	spray	2.8	0.26		7
Legumes	Cyprus	WP WG			0.15-0.20		7
Legumes	Panama	WP		1.6			
Lentil	Hungary	WG		1.1	0.19		21
Lettuce	Australia	WP WG	spray	1.8	0.16		7
Lettuce	Mozambique	WP					
Lettuce, cos	Paraguay	WP	spray	0.005		2	
Lettuce, head	France	WG		1.4			
Lettuce, head	Germany	WG	spray	0.84		1-2	21
Lettuce, head	Germany	WP	spray	0.96		1	21
Lettuce, head	Germany	WP	dry dressing			1	2
Lettuce, head	Greece	WP WG	spray	1.4			
Lettuce, head	Malaysia	WP WG					14
Maize	Bolivia	WG	spray	1.4	0.47	2-3	
Maize	Costa Rica	WP WG	spray		0.12-0.16		7
Maize	Dominican	WG	spray				7
Maize	Paraguay	WP	spray				
Maize	Peru	WP	spray			3-6	7
Maize	Peru	WG		0.80		2-3	7
Mango	Egypt	WG	spray	6.4	0.32	1-3	
Mango	Mozambique	WP					
Melon	Bolivia	WG	spray	1.4	0.23	3-15	
Melon	Costa Rica	WP WG	spray	1.6	1.6		7
Melon	Dominican	WG	spray	1.4			7
Melon	Israel	WG		2.0			5
Melon	Mozambique	WP					
Melon	Paraguay	WP	spray			2	
Melon	Zimbabwe	WP					14
Nectarine	Zimbabwe	WP					14
Onion	Bolivia	WG	spray	1.4	0.47	3-6	
Onion	Costa Rica	WP	spray	1.4			
Onion	Costa Rica	WP WG	spray	1.6	1.6		7
Onion	Dominican	WG	spray	1.4			7
Onion	Israel	WG		2.0			10

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Onion	Mozambique	WP					
Onion	Paraguay	WP	spray			2	
Onion	Peru	WG		0.80	0.13	1	7
Onion	Poland	WP		1.6			
Onion	Rumania	WP WG					
Pea	Argentina	WG	spray		0.16		10
Pea	Argentina	WP	spray				10
Peach	Bolivia	WG	spray		0.20	2-4	
Peach	Greece	WP WG	spray				
Peach	Mozambique	WP					
Peach	Paraguay	WP	spray			2-4	
Peach	Portugal	WP	spray				7
Peach	Sth Africa	WP	spray		0.16		14
Peach	Uruguay	WP	spray	3.6	0.24	3	25
Peach	Zimbabwe	WP					14
Peanut	Costa Rica	WP WG	spray		0.096-0.16		
Peanut	Dominican	WG	spray				
Peanut	Greece	WP WG	spray				
Peanut	Mozambique	WP					
Peanut	Panama	WP					
Peanut	Paraguay	WP	spray				
Pear	Argentina	WP	spray			1-4	20
Pear	Argentina	WG	spray		0.12-0.16	4	20
Pear	Australia	WP WG	spray		0.12-0.16		14
Pear	Belgium	WP	spray				10
Pear	Bolivia	WG	spray		0.15-0.20	6-10	
Pear	Chile	WG	spray			7-10	14
Pear	Denmark	WP	mist	1.75			28
Pear	Greece	WP WG	spray				
Pear	Italy	WP WG	spray		0.10-0.14		28
Pear	Morocco	WP	spray				14
Pear	Mozambique	WP					
Pear	Netherlands	WG	mist				28
Pear	Netherlands	WP	spray	1.8	0.16	7-10	28
Pear	Netherlands	WP	mist			5	28
Pear	New Zealand	WG	spray		0.07-0.11	10	14
Pear	Paraguay	WP	spray				
Pear	Poland	WP					35
Pear	Portugal	WP WG	spray		0.14		7
Pear	Rumania	WP WG					
Pepper, sweet	Argentina	WP					3
Peppers, sweet	Hungary	WG	greenhouse	1.4	0.23		7
Peppers, sweet	Spain	WP	spray		0.12-0.16		15
Pistachio	Argentina	WP	spray				
Plum	Germany	WG	spray		0.12	1-4	28
Plum	Germany	WP	spray		0.12	4	28
Plum	Greece	WP WG	spray				
Plum	Paraguay	WP	spray			2-4	
Plum	Sth Africa	WP	spray		0.16		14
Plum	Uruguay	WP	spray	3.6	0.24	3	25
Pome fruits	Belgium	WG	spray				14
Pome fruits	Cyprus	WP WG			0.15-0.20		7
Pome fruits	Czech	WP					21
Pome fruits	Germany	WG	spray		0.12	1-12	28
Pome fruits	Luxembourg	WG	mist				14
Pome fruits	Spain	WP WG	spray	2.4	0.12-0.16	1	15
Pome fruits	Switzerland	WP	spray				21

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Potato	Argentina	WG	spray		0.14-0.19		7
Potato	Argentina	WP	spray	1.4	0.34		7
Potato	Argentina	WP					3
Potato	Australia	WP WG	spray		0.12-0.16		7
Potato	Austria	WP	spray	1.7	0.29	3	14
Potato	Belgium	WG	spray	2.8			14
Potato	Bolivia	WG	spray	1.3	0.42	5-15	
Potato	Canada	WG	spray	1.8	3.3		1
Potato	Canada	DP	spray	2.3			1
Potato	Canada	DP	dry dressing			1-2	
Potato	Chile	WG	spray	1.8			
Potato	Costa Rica	WP WG	spray	2.0			7
Potato	Croatia	WP		1.6			14
Potato	Cyprus	WP WG			0.15-0.20		7
Potato	Czech	WP		1.6			7
Potato	Dominican	WG	spray	1.8			7
Potato	Ecuador	WP	spray	2.0	0.50	2-3	14
Potato	France	WP WG	spray	1.4	0.27-0.40		
Potato	Germany	WP	spray	1.4		4	14
Potato	Germany	WG	spray	1.3		1-5	14
Potato	Greece	WP WG	spray	1.4			
Potato	Guatemala	WG					
Potato	Hungary	WG		1.3	0.25		21
Potato	Indonesia	WP	spray	0.64	0.16		
Potato	Ireland	WG	spray	1.4	0.64		
Potato	Luxembourg	WG	spray	2.8			14
Potato	Macedonia	WP		1.6			14
Potato	Mozambique	WP					
Potato	Netherlands	WG	spray	1.7			
Potato	Netherlands	WP	spray	2.9			
Potato	Pakistan	WP					
Potato	Paraguay	WP	spray			2	
Potato	Peru	WP	spray	1.2		3-4	7
Potato	Peru	WP		0.55	0.092	2-4	7
Potato	Peru	WG		0.80		3-6	7
Potato	Poland	WP		1.4			14
Potato	Portugal	WP WG	spray		0.14		7
Potato	Rumania	WP WG		1.4			
Potato	Spain	WP	spray		0.12-0.16		15
Potato	Sth Africa	WP	spray	3.2	0.24		
Potato	Switzerland	WP	spray	3.2			21
Potato	Switzerland	WG	spray	2.4			
Potato	Tunisia	WP	spray			3-4	
Potato	UK	WP	spray	1.4	0.70		7
Potato	UK	WG	spray	1.6			7
Potato	Uruguay	WP	spray	1.4	0.36	8-15	25
Potato	USA	WP WG	spray	1.8	1.3	7	3, 14
Potato	Yugoslavia	WP		1.6			14
Potato	Zimbabwe	WP					3
Prunes	Sth Africa	WP	spray		0.16		14
Pumpkin	Bolivia	WG	spray	1.4	0.23	3-15	
Pumpkin	Costa Rica	WP	spray	1.4			
Rape	Argentina	WP	dry dressing				
Rape	Ireland	WG	spray	1.4	0.64		
Rape, winter	UK	WG	spray	1.6			GS[1]
Rape, winter	UK	WP	spray	1.4	5.6	1	GS[1]
Rice	Costa Rica	WG		1.6			7

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Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Rice	Dominican	WG	spray	1.4			7
Soya beans	Hungary	WG		1.1	0.28		21
Stone fruits	Argentina	WP	spray			1-4	14
Stone fruits	Argentina	WG	spray		0.16-0.32		10
Stone fruits	Australia	WP	spray		0.12	3-4	21
Stone fruits	Cyprus	WP WG			0.15-0.20		7
Stone fruits	Germany	WP	spray		0.12	4	21
Stone fruits	Spain	WP WG	spray	2.4	0.12-0.16	1	15
Strawberry	Belgium	WP	spray				14
Strawberry	Costa Rica	WP	spray				
Strawberry	Cyprus	WP WG			0.15-0.20		7
Strawberry	Greece	WP WG	spray				
Strawberry	Luxembourg	WP	spray	0.010	0.005		14
Strawberry	Paraguay	WP	spray				
Strawberry	Spain	WP	spray	2.4	0.12-0.16	1-6	15
Sugar beet	Bulgaria	WP	seed treat				
Sugar beet	Canada	WG	spray	1.8			21
Sunflower	Macedonia	WP		1.6			
Sunflower	Rumania	WG		1.1			
Sunflower	Yugoslavia	WP		1.6			
Sweet corn	Greece	WP WG	spray				
Tomato	Argentina	WG	spray		0.14-0.19		10
Tomato	Argentina	WP	spray				10
Tomato	Australia	WP WG	spray	1.8			2
Tomato	Belgium	WG	spray		0.16		14
Tomato	Belgium	WG	spray, greenhouse		0.16		3
Tomato	Canada	DP	spray	3.9			7
Tomato	Canada	WG	spray	2.6			7
Tomato	Chile	WG	spray	1.8			
Tomato	Costa Rica	WP WG	spray	2.4			7
Tomato	Croatia	WP		2.4			14
Tomato	Dominican	WG	spray	1.8			5
Tomato	Ecuador	WP	spray	2.4	0.16	1-4	5
Tomato	France	WG		1.4			
Tomato	Germany	WP	spray	2.9		1-4	5
Tomato	Germany	WP	dry dressing			1	2
Tomato	Greece	WP WG	spray	1.4			
Tomato	Hungary	WG	greenhouse	1.4	0.23		7
Tomato	Indonesia	WP	spray	0.64	0.16		
Tomato	Italy	WP WG	spray		0.10-0.14		28
Tomato	Luxembourg	WG	spray				14
Tomato	Luxembourg	WG	spray greenhouse				3
Tomato	Macedonia	WP		2.4			14
Tomato	Malaysia	WP WG					14
Tomato	Morocco	WG					30
Tomato	Mozambique	WP					
Tomato	Pakistan	WP					
Tomato	Paraguay	WP	spray	0.005		2	
Tomato	Peru	WG		0.80	0.13	3-6	7
Tomato	Poland	WP					5
Tomato	Portugal	WP WG	spray		0.14		7
Tomato	Rumania	WP WG					
Tomato	Spain	WP	spray		0.12-0.16		15
Tomato	Sth Africa	WP	spray	3.2	0.24		3
Tomato	Tunisia	WP	spray	1.2	0.20		

Crop	Country	Form	Application				PHI, days
			Method	Max rate, kg ai/ha	Spray conc, kg ai/hl	No.	
Tomato	Turkey	WG	spray	0.56	0.14	2-3	5
Tomato	Uruguay	WP	spray	1.4	0.36	8-15	25
Tomato	Yugoslavia	WP		2.4			14
Tomato	Zimbabwe	WP					3
Vegetables	Angola	WP	spray	0.50	0.20		
Vegetables	Argentina	WP	spray				10
Vegetables	Cyprus	WP WG			0.15-0.20		7
Vegetables	Jordan	WP	spray	1.2	0.2	1-3	
Vegetables	Saudi Arabia	WP	spray	0.80	0.20	1-3	
Vegetables	Spain	WP WG	spray	2.4	0.12-0.16	1-6	15
Vegetables	Tunisia	WP	spray				
Watermelon	Bolivia	WG	spray	1.4	0.23	3-15	
Watermelon	Malaysia	WP WG					14
Wheat, winter	Ireland	WG	spray	1.4	0.64	1-2	42
Wheat, winter	UK	WP	spray	1.4	0.56	1-2	42

[1] GS: early growth stage, final application in December.

RESIDUES RESULTING FROM SUPERVISED TRIALS

The results of supervised trials on horticultural and agricultural crops are shown in Tables 19-41.

Table 19. Apples. Germany.
Table 20. Apples. Australia, Brazil, Canada, Hungary, Italy, the UK.
Table 21. Pears. Germany.
Table 22. Stone fruit. Australia, Germany.
Table 23. Grapes. Austria, Germany, France, Hungary, Italy.
Table 24. Strawberries. Germany, Switzerland, the UK.
Table 25. Berry fruits. the UK.
Table 26. Currants. Germany.
Table 27. Bananas. Australia.
Table 28. Cabbage. Germany.
Table 29. Cauliflower. Germany.
Table 30. Cucumber. Hungary, the UK.
Table 31. Tomatoes. France, Germany, Hungary.
Table 32. Lettuce. Australia, France, Germany.
Table 33. Beans. Germany.
Table 34. Peas. Germany.
Table 35. Potatoes. Belgium, Germany.
Table 36. Celery. Germany.
Table 37. Wheat. Germany, Hungary.
Table 38. Rape seed. the UK.
Table 39. Hops. Germany.
Table 40. Wheat forage. Germany.
Table 41. Wheat fodder. Germany, Hungary.

Metiram-complex is the old name for technical material and contains 89% metiram. Old labels and use patterns quoting 80% ai are equivalent to modern labels quoting 70% ai. A different factor (2.09) is now used to calculate the metiram residue from the carbon disulfide content; formerly the factor was 2.35. Most of the application rates and spray concentrations in the trials are quoted on the old (metiram-complex) basis. The difference should be taken into account when comparing trials data with

modern labels.

Where residues were not detected, they are recorded in the Tables as less than the limit of determination (LOD), eg <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. Only when residues were detected in control samples are they recorded in the Tables. This rarely happened.

Most of the trials were reported on detailed summary sheets. For many of them it was not clear whether the reported residues had or had not been adjusted for the analytical recovery. Recoveries were generally good, so there would be little difference between adjusted and unadjusted residues. ETU recoveries tended to be a little low, around 70%.

Dithiocarbamate residues are expressed as mg CS_2/kg throughout the tables and text. EBDC is used as an abbreviation for ethylenebisdithiocarbamates. ETU residues were determined in most of the trials.

Plot sizes in German apple trials ranged from 3 trees to 0.4 ha but were commonly 10-20 trees. The type of sprayer was not always recorded but the use of compressed air sprayers and atomizers is reported.

In the Canadian apple trials the trees were sprayed by hand gun and the plot size was 16 trees. Commercial sprayers or mistblowers were used in the UK apple trials where the plot size was 1 acre. The plot size in the Italian apple trials was 0.5 ha.

Plot sizes in the German trials on stone fruits and pears ranged from 4 trees to 160 m^2.

Compressed air sprayers and atomizers were used in the German grape trials where the plot size ranged from 15 to 400 m^2. Plot sizes in the French trials were 45 to 270 vines.

Mistblowers and HV sprayers were used in the UK strawberry trials where plot sizes ranged from 20 m^2 to 2 ha. In Germany strawberry trials were conducted on 20-25 m^2 plots. Plot sizes in German currant trials were 5-12 bushes, and in UK gooseberry trials 0.25-1 ha.

Plot sizes in the German vegetable trials were commonly 5-50 m^2. Compressed air sprayers were used for foliar application.

German supervised trials on hops were with plots of 1000 plants or 0.2-0.9 ha.

Table 19. Residues in apples from foliar applications of metiram in supervised trials in Germany. Underlined residues are from treatments according to GAP.

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
1971 (Cox's Orange)	WP		0.2	10	30	1.2		2221 F71/7E
1973 (James Grieves)	WP	3.2	0.32	3	0 3 5 7 10 14	0.7 0.6 - 0.2 <0.2 <0.2	 <0.01	2221 F73/16A
1973 (Cox's Orange)	WP	3.2	0.32	3	0 3	0.3 <0.2		2221 F73/27A

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
					6	0.2		
					10	0.4		
					14	0.4	0.04	
1973 (James Grieves)	WP	3.2	0.32	3	0	0.6		2221 F73/15A
					3	0.6		
					5	0.3		
					7	0.3		
					10	<0.2		
					14	0.2	<0.01	
1973 (Golden Delicious)	WP	3.2	0.32	3	0	0.8		2221 F73/26A
					3	1.1		
					6	0.7		
					8	0.9		
					10	<0.2		
					14	1.7	0.01	
1973 (Golden Delicious)	WP	3.2	0.32	3	0	0.2		2221 F73/25A
					3	0.8		
					6	0.5		
					8	0.9		
					10	<0.2		
					14	0.2	0.02	
1973 (Jonathan)	WP	3.2	0.32	3	0	0.6		2221 F73/29A
					3	1.0		
					6	0.5		
					8	0.7		
					10	0.4		
					14	<0.2	0.03	
1973 (Cox's Orange)	WP	3.2	0.32	3	0	0.6		2221 F73/28A
					3	0.3		
					6	0.2		
					10	<0.2		
					14	0.3	0.05	
1975 (Cox's Orange)	WP	3 × 3.2+ 11 × 2.4	3 × 0.16+ 11 × 0.12	14	0	1.1	0.15	22201 F75/5A
					4	0.31	0.23	
					7	0.42	0.08	
					10	0.29	0.04	
					14	<0.05	0.03	
					21	0.16	0.03	
1975 (James Grieve)	WP	3 × 3.2 +11 × 2.4	3 × 0.2 +11 × 0.15	14	0	2.6		22201 F75/6A
					4	0.73		
					7	0.93		
					10	0.69		
					14	1.00		
					21	0.40		
1975 (James Grieve)	WP	3 × 3.2+ 11 × 2.4	3 × 0.2+ 11 × 0.15	14	0	1.1		22201 F75/7A
					4	1.5		
					7	0.12		
					10	0.69		
					14	0.76		
					21	0.60		
1975 (Cox's Orange)	WP	3 × 3.2+ 11 × 2.4	3 × 0.2+ 11 × 0.15	14	0	3.0		22201 F75/8A
					4	2.3		
					7	0.59		
					10	0.32		
					14	0.54		
					21	0.10		
1976 (Cox's orange)	WP	2 × 1.6+ 11 ×	2 × 0.1+ 11 ×	13	7	2.5	0.04	2220 F76/20A

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
		2.4	0.15		14	2.2	0.04	
1976 (Jonathan)	WP	2 × 1.6+ 14 × 2.4	2 × 0.10+ 14 × 0.15	16	7 14		0.03 0.02	22201 F76/27A
1976 (Lody)	WP	2 × 1.6+ 5 × 2.4	2 × 0.1+ 5 × 0.15	7	35	<0.05	0.01	22201 F76/1E
1976 (Cox's Orange)	WP	2.4	0.15	12	7 14	1.8 1.9	0.03 <.01	22201 F76/26A
1976 (Jonathan)	WP	2.4	0.15	12	7 14	1.2 1.6	0.02 0.03	22201 F76/25A
1976 (James Grieve)	WP	2 × 1.6+ 8 × 2.4	2 × 0.1+ 8 × 0.15	10	15		0.02	22201 F76/2E
1976 (Golden Delicious)	WP	2.4	0.15	12	7 14	3.2 3.0	0.02 0.03	22201 F76/24A
1976 (Golden Delicious)	WP	3 × 2.4+ 12 × 1.8	3 × 0.12+ 12 × 0.09	15	0 7 14 19 28	8.7 0.49 0.16 0.35 0.26	0.05 0.02 0.01 0.01 0.01	22201 F76/23A
1976 (Jonathan)	WP	3 × 3.2+ 12 × 2.4	3 × 0.20+ 12 × 0.15	15	0 7 14 21 28	2.5 2.6 3.1 1.6 2.0	0.07 0.02 0.02 0.02 0.01	22201 F76/21A
1977 (Golden Delicious)	WP	1.2	0.06	19	0 7 14 21 28	0.80 0.50 0.70 0.70 0.60	0.02 0.01 <0.01 <0.01 <0.01	28802 F77/1A
1977 (Golden Delicious)	WP	1.2	0.06	19	0 7 14 21 28	0.60 0.80 0.70 0.40 0.30	0.02 0.01 <0.01 <0.01 <0.01	28802 F77/3A
1977 (Cox's Orange)	WP	1.2	0.06	19	0 7 14 21 28	1.0 0.50 0.80 0.50 0.80	0.02 0.02 0.01 <0.01 0.01	28802 F77/2A
1977 (Jonathan)	WP	0.9	0.045	11	0 7 14 21 28	1.1 0.80 0.50 0.30 0.40	0.03 0.01 <0.01 <0.01 <0.01	28802 F77/6A
1977 (Goldparmäne)	WP	0.9	0.045	11	0 7 14 21 28	1.0 1.3 0.50 0.40 0.70	0.02 0.01 <0.01 0.01 <0.01	28802 F77/4A
1977 (Golden Delicious)	WP	0.9	0.045	11	0 7 14 21 28	1.0 0.50 0.50 0.30 0.40	0.03 0.02 <0.01 <0.01 0.01	28802 F77/5A
1979 (Golden	WP	3 × 2.4+ 12 ×	3 × 0.16+ 12	15	21	0.29	0.01	22201 F79/4E

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
Delicious)		1.8	× 0.12					
1979 (Golden Delicious)	WP	3 × 2.4+ 12 × 1.8	3 × 0.16+ 12 × 0.12	15	21	0.25	<0.01	22201 F79/3E
1979 (Boskoop)	WP	4 × 2.4+ 11 × 1.8	4 × 0.16+ 11 × 0.12	15	21	0.42	<0.01	22201 F79/7E
1979 (Boskoop)	WP	4 × 2.4+ 11 × 1.8	4 × 0.16+ 11 × 0.12	15	21	0.43	<0.01	22201 F79/8E
1979 (Melrose)	WP	3 × 2.4+ 12 × 1.8	3 × 0.16+ 12 × 0.12	15	21	0.37	<0.01	22201 F79/6E
1979 (Melrose)	WP	3 × 2.4+ 12 × 1.8	3 × 0.16+ 12 × 0.12	15	21	0.48	0.01	22201 F79/5E
1980 (James Grieve)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0 7 14 21 28	2.1 1.8 0.64 0.93 0.63	0.02 0.04 0.02 0.02 0.02	22201 F80/12A
1980 (Golden Delicious)	WP	2 × 2.4+ 12 × 1.8	2 × 0.16+12 × 0.12	14	0 7 14 21 28	1.3 1.2 0.58 0.79 0.58	0.02 0.02 0.01 0.01 0.01	22201 F80/11A
1982 (James Grieve)	WP	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0 14 21 28 35	0.60 0.10 0.10 0.06 <0.02	0.02 0.02 <0.01 <0.01 <0.01	22201 F82/5A
1982 (Jonathan)	WP	2.3	0.12	10	0 14 21 28 35	1.8 1.6 0.89 0.70 0.78	0.09 0.04 0.03 0.04 0.02	22201 F82/3A
1982 (Cox's Orange)	WP	1.8	0.12	10	0 14 21 28 35	1.6 1.0 0.63 0.60 0.57	0.02 0.01 0.01 0.01 0.01	22201 F82/6A
1982 (Gravensteiner)	WP	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0 14 21 28 35	0.10 0.07 0.06 0.02 0.03	<0.01 <0.01 <0.01 <0.01 <0.01	22201 F82/4A
1983 (Melrose)	WP	1.8	0.24	8	0 28 35 42 49	1.7 0.45 0.16 0.28 0.14	0.02 0.01 <0.01 <0.01 <0.01	22201 F83/5A
1983 (James Grieve)	WP	1.8	0.12	8	0 28 35 42 49	1.6 0.07 0.10 0.12 0.04	0.07 <0.01 <0.01 <0.01 <0.01	22201 F83/7A
1983 (Golden Delicious)	WP	1.8	0.12	8	0 28 35 42	1.8 0.21 0.10 0.14	0.06 0.01 <0.01 <0.01	22201 F83/4A

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
					49	0.22	<0.01	
1983	WP	2.3	0.12	8	0 28 35 42 49	2.7 1.5 0.32 0.42 0.20	0.13 0.03 0.02 0.02 <0.01	22201 F83/6A
1988 (Gloster)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 35 42 49 56	2.4 0.82 0.69 0.35 0.77	0.04 <0.02 <0.02 <0.02 <0.02	22226 F88/8A
1988 (Cox's Orange)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0 35 42 49 56	0.12 0.32 0.10 0.18 0.37	0.03 <0.02 <0.02 <0.02 <0.02	22226 F88/9A
1988 (Gloster)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 21 28 35 42	2.9 0.57 1.0 0.38 0.52	0.04 <0.02 <0.02 <0.02 <0.02	22228 F88/3A
1988 (Jonagold)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0 35 42 49 56	1.3 0.38 0.16 0.23 0.84	0.03 <0.02 <0.02 <0.02 <0.02	22226 F88/10A
1988 (Cox's Orange)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0 21 28 35 42	2.1 0.32 0.27 0.62 0.19	<0.02 <0.02 <0.02 <0.02 <0.02	22226 F88/4A
1988 (Gloster)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 35 42 49 56	3.1 0.54 0.67 0.20 0.66	0.03 <0.02 <0.02 <0.02 <0.02	22226 F88/8A
1988 (Jonagold)	WP	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0 21 28 35 42	1.1 0.24 0.24 2.0 0.83	<0.02 <0.02 <0.02 <0.02 <0.02	22226 F88/5A
1988 (Jonagold)		4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 21 28 35 42	2.1 0.83 0.71 1.1 0.16	<0.02 0.03 0.03 <0.02 0.03	22226 F88/2A
1988 (Alkmene)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 21 28	4.2 1.4 0.76	0.04 0.04 0.03	22226 F88/1A
1988 (Alkmene)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 35 42 49 56	3.2 0.83 0.28 0.69 0.44	0.03 0.04 0.04 0.03 <0.02	22226 F88/6A
1988 (Jonagold)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 35	2.7 0.36	0.02 <0.02	22226 F88/7A

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
					42	0.22	<0.02	
					49	0.36	0.02	
					56	0.22	0.03	
1988 (Gloster)	WP	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0	2.5	0.09	22226 F88/3A
					21	0.92	0.02	
					28	1.9	<0.02	
					35	0.50	<0.02	
					42	0.40	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	2.4	<0.02	22228 F88/14A
					49	0.21	<0.02	
					56	0.10	<0.02	
					63	0.06	<0.02	
					70	0.12	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.8	0.03	22228 F88/10A
					35	0.23	<0.02	
					42	0.19	<0.02	
					49	0.14	<0.02	
					56	0.41	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.3	<0.02	22228 F88/5A
					21	0.37	<0.02	
					28	0.26	<0.02	
					35	1.6	<0.02	
					42	0.39	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.9	0.02	22228 F88/9A
					35	0.14	<0.02	
					42	0.11	<0.02	
					49	0.16	<0.02	
					56	-	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 10 × 1.8	4 × 0.16+ 10 × 0.12	14	0	1.7	<0.02	22228 F88/4A
					21	0.12	<0.02	
					28	0.27	<0.02	
					35	0.16	<0.02	
					42	0.30	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	1.3	0.03	22228 F88/15A
					49	0.18	<0.02	
					56	0.11	<0.02	
					63	0.21	<0.02	
					70	0.12	<0.02	
1988 (Cox's orange)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	0.91	<0.02	22228 F88/24A
					35	0.18	<0.02	
					42	0.16	<0.02	
					49	0.10	<0.02	
					56	0.13	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0	1.4	0.03	22228 F88/20A
					35	0.22	<0.02	
					42	0.08	<0.02	
					49	0.08	<0.02	
					56	0.12	<0.02	
1988 (Cox's Orange)	WG	4 × 2.4+ 8 × 1.8	4 × 0.16+ 8 × 0.12	12	0	1.1	<0.02	22228 F88/19A
					35	0.12	<0.02	
					42	0.11	<0.02	
					49	0.05	<0.02	
					56	0.18	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 6 × 1.8	4 × 0.16+ 6 × 0.12	10	0	0.73	0.02	22228 F88/25A
					35	0.20	<0.02	
					42	0.10	<0.02	
					49	0.11	<0.02	

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
					56	0.20	<0.02	
1988 (Alkmene)	WG	4 × 2.4+ 8 × 1.8	4 × 0.32+ 8 × 0.24	12	0	4.7	<0.02	22228 F88/16A
					35	0.81	<0.02	
					42	0.54	0.04	
					49	0.71	0.02	
					56	0.18	0.04	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0	2.0	0.05	22228 F88/7A
					35	0.20	<0.02	
					42	0.24	<0.02	
					49	0.19	<0.02	
					56	0.11	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0	2.0	0.02	22228 F88/2A
					21	0.62	0.03	
					28	0.67	<0.02	
					35	0.37	<0.02	
					42	0.59	0.04	
1988 (Gloster)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0	1.6	<0.02	22228 F88/23A
					35	0.33	<0.02	
					42	0.19	<0.02	
					49	0.29	<0.02	
					56	0.13	<0.02	
1988 (Gloster)	WG	4 × 2.4+ 8 × 1.8	4 × 0.32+ 8 × 0.24	12	0	2.0	<0.02	22228 F88/18A
					35	0.38	<0.02	
					42	0.22	<0.02	
					49	0.26	<0.02	
					56	0.24	<0.02	
1988 (Gloster)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0	2.8	0.04	22228 F88/13A
					49	0.19	<0.02	
					56	0.32	<0.02	
					63	0.21	<0.02	
					70	0.34	<0.02	
1988 (Alkmene)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0	5.7	0.10	22228 F88/11A
					49	0.18	<0.02	
					56	0.27	<0.02	
					63	0.18	<0.02	
					70	0.21	<0.02	
1988 (Jonagold)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0	2.0	0.18	22228 F88/22A
					35	0.39	<0.02	
					42	0.19	<0.02	
					49	0.10	<0.02	
					56	0.13	<0.02	
1988 (Alkmene)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0	3.4	0.08	22228 F88/1A
					21	1.3	0.02	
					28	1.1	0.05	
					35	0.77	0.03	
					42	1.2	0.03	
1988 (Alkmene)	WG	4 × 2.4+ 6 × 1.8	4 × 0.32+ 6 × 0.24	10	0	3.7	0.03	22228 F88/21A
					35	0.64	<0.02	
					42	0.67	0.03	
					49	0.62	<0.02	
					56	0.51	0.04	
1988 (Alkmene)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0	4.5	0.05	22228 F88/6A
					35	0.78	0.02	
					42	0.23	0.02	
					49	0.33	0.02	
					56	0.66	<0.02	

Year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
1988 (Jonagold)	WG	4 × 2.4+ 8 × 1.8	4 × 0.32+ 8 × 0.24	12	0 35 42 49 56	0.64 0.25 0.16 0.12 0.19	0.06 <0.02 <0.02 <0.02 <0.02	22228 F88/17A
1988 (Jonagold)	WG	4 × 2.4+ 10 × 1.8	4 × 0.32+ 10 × 0.24	14	0 49 56 63 70	3.3 0.17 0.68 0.12 0.05	0.09 <0.02 <0.02 <0.02 <0.02	22228 F88/12A

Table 20. Residues in apples from foliar applications of metiram in supervised trials in Australia, Brazil, Canada, Hungary, Italy and the UK. Underlined residues are from treatments according to GAP

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
Australia (Vic), 1977 (Granny Smith)	WP	3.6	0.2	8	18 24 28 118	1.9 2.1 1.6 0.20	0.03 0.03 0.02 <0.01	37900 F77/2A
Australia (Vic), 1977 (Jonathan)	WP	3.6	0.2	8	10 15 21 28 71	2.6 2.0 0.8 1.0 0.05	0.03 0.03 <0.01 <0.01 <0.01	37900 F77/1A
Brazil, 1986 (Fuji)	WP	2.4	0.3	1	32	0.16	<0.01	22226 F86/2E
Brazil, 1986 (Fuji)	WP	1.2	0.15	1	32	<0.02	<0.01	22226 F86/1E
Canada, 1977 (Red Delicious)	WP	2.2	0.25	15	88	0.2, 0.3, 0.4, 0.4	<0.01 (4)	37900 F77/7E
Canada, 1977 (McIntosh)	WP	2.2	0.25	15	88	0.5, <0.05 (2), 0.2	<0.01 (4)	37900 F77/19E
Canada, 1977 (Golden Delicious)	WP	2.2	0.25	15	88	0.5, 0.2, <0.05, 0.4	<0.01, 0.02, <0.01, 0.01	37900 F77/11E
Canada, 1977 (Red Delicious)	WP	2.2	0.25	15	88	0.2, 0.3, 0.4, 0.4	<0.01 (4)	37900 F77/7E
Canada, 1977 (Spartan)	WP	2.2	0.25	15	88	0.3, 0.3, 0.1, 0.1	<0.01 (4)	37900 F77/15E
Hungary, 1990	DF	2.4	0.24	14 15	7 0 3 7 10 14 30 41	0.70, 0.17, 0.39 1.9, 1.7, 1.4 2.4, 0.87, 0.67 1.3, 0.59, 0.39 0.70, 0.78, 0.42 0.73, 0.47, 0.26 0.12, 0.1, 0.18, 0.1, 0.20 0.18, 0.45, 0.27, 0.18, 0.17		90/10604
Italy, 1990 (Jonagold)	WP	1.2	0.16	4	43	0.34	<0.02	22201 F90/1E
Italy, 1990 (Jonagold)	WP	1.2	0.16	5	29	0.15	<0.02	22201 F90/2E
Italy, 1990 (Cooper 7SB2)	WP	2.4	0.16	18	0 7	3.6 3.3	0.16 0.11	22201 F90/3A

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
					14 20 27 35 42	2.7 2.0 2.1 1.3 2.6	0.15 0.04 0.05 0.05 0.06	
Italy, 1990 (Golden Delicious)	WP	1.1	0.15	7	19	0.15	<0.02	22201 F90/3E
Italy, 1990 (Imperatore Dallago)	WP	2.9	0.16	17	0 7 14 21 28 35 42	1.6 0.82 0.62 0.62 0.67 0.62 0.48	0.02 0.02 <0.02 <0.02 <0.02 <0.02 <0.02	22201 F90/5A
Italy, 1990 (Golden Delicious)	WP	1.1	0.16	6	46	0.14	<0.02	22201 F90/4E
Italy, 1990 (Golden Delicious)	WP	1.9	0.16	15	0 7 14 21 28 35 42	2.2 0.95 0.69 0.88 0.34 0.24 0.10	0.02 0.03 <0.02 <0.02 <0.02 <0.02 <0.02	22201 F90/4A
UK, 1976 (Cox's Orange Pippin)	WP	3.2	0.57	7	47 55	0.57 0.34		37900 F76/5A1
	WP	3.2	0.57	8	18 29	0.27 0.30		37900 F76/9E1 F76/6A1
UK, 1976 (Golden Delicious)	WP	3.2	0.57	4	37 57	0.25 0.28		37900 F76/10E1 F76/7A1
UK, 1976 (Cox's Orange Pippin)	WP	3.2	0.57	9	42 61	0.52 0.13		37900 F76/11E1 F76/8A1
	WP	0.04	0.005	6	7 14	<0.05 <0.05	<0.01 <0.01	37901 F79/1A
	WP	0.04	0.007	8	7 15	<0.05 <0.05	<0.01 <0.01	37901 F79/2A
	WP	0.04	0.007	9	7 15	<0.05 <0.05	<0.01 <0.01	37901 F79/3A
	WP	0.02	0.04	21	9 18	0.02 <0.02	<0.01 <0.01	37901 F79/7A
	WP	0.04	0.007	8	7 14	<0.02 <0.02	<0.01 <0.01	37901 F79/8A
	WP	0.04	0.012	8	19	0.03	0.01	37901 F79/1E
UK, 1980 (Cox's Orange Pippin)	WP	0.019	0.004	17	7	<0.02	<0.01	37901 F80/1E
	WP	0.019	0.003	19	6	<0.02	<0.01	37901 F80/3E
	WP	0.019	0.006	17	7	<0.02	<0.01	37901 F80/2E
UK, 1981 (Cox's Orange Pippin)	WP	0.02-0.04	0.011	10	7	0.04	<0.01	37901 F81/2E
	WP	0.004-0.01	0.016	19	7	0.05	<0.01	37901 F81/3E
UK, 1982 (Cox's Orange Pippin)	WP	0.038	0.014	10	14	<0.02	<0.01	37901 F82/1E
	WP	0.035	0.010	6	14	0.08	<0.01	37901 F82/2E

Table 21. Residues in pears from foliar applications of metiram WP in supervised trials in Germany. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
1983 (Williams Christ)	1.8	0.12	8	0	1.3	0.05	22201
				28	0.49	0.03	F83/8A
				35	0.29	<0.01	
				42	0.21	0.02	
				49	0.21	<0.01	
1983 (Conference)	1.8	0.24	8	0	3.9	0.10	22201
				28	0.37	0.03	F83/9A
				35	0.47	<0.01	
				42	0.33	<0.01	
				49	0.32	<0.01	
1982 (Williams Christ)	1.8	0.12	10	0	0.93	0.02	37900
				14	0.37	0.01	F82/1A
				21	0.49	<0.01	
				28	0.24	0.01	
				35	0.22	<0.01	
1983 (Williams Christ)	1.8	0.12	8	0	0.75	0.05	37900
				28	0.36	0.02	F83/5A
				35	0.11	<0.01	
				42	0.11	<0.01	
				49	0.12	<0.01	
1983 (Conference)	1.8	0.24	8	0	2.0	0.05	37900
				28	0.53	0.02	F83/6A
				35	0.29	0.02	
				42	0.18	<0.01	
				49	0.11	<0.01	

Table 22. Residues in apricots, cherries, peaches and plums from foliar applications of metiram WP in supervised trials in Australia and Germany. Underlined residues are from treatments according to GAP.

STONE FRUIT Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
APRICOTS							
Australia (SA), 1980	0.12	0.12		1	5.6		80/10200
				3	3.7		
				5	5.6		
				7	4.3		
Australia (SA), 1980	0.16	0.16		1	3.3		80/10200
				3	3.9		
				5	1.6		
				7	2.3		
CHERRIES							
Australia (SA), 1980	0.12	0.12		1	3.5		80/10200
				3	2.6		
				5	2.6		
				7	2.4		
Australia (SA), 1980	0.16	0.16		1	5.0		80/10200
				3	4.0		

STONE FRUIT Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
				5 7	5.2 2.7		
Germany, 1976 (Schattenmorelle)	3.2	0.16	4	0 7 14 21 28	1.9 1.6 0.50 0.24 0.50	0.04 0.02 0.02 0.02 0.01	22201 F76/12A
Germany, 1973 (Schattenmorelle)	3.2	0.16	4	0 5 7 11 14 21	8.5 4.3 3.6 1.3 1.0 1.0	 0.5	2221 F73/1A
Germany, 1973 (Schattenmorelle)	3.2	0.16	4	0 5 7 11 14 21	9.1 5.0 2.3 1.0 1.0 0.7	 0.02	2221 F73/2A
Germany, 1976 (Schattenmorelle)	3.2	0.16	4	0 7 14 21 28	4.0 1.7 <0.05 1.0 <0.05	0.07 0.03 0.03 0.03 <0.01	22201 F76/13A
PEACHES							
Australia (SA), 1980	0.12	0.12		1 3 5 7	7.2 2.2 2.3 1.2		80/10200
Australia (SA), 1980	0.16	0.16		1 3 5 7	9.1 8.4 5.7 4.3		80/10200
Australia (Qld), 1980	0.12	0.12		1 3 5 7	5.9 4.8 4.6 3.2		80/10200
Australia (Qld), 1980	0.24	0.24		1 3 5 7	6.6 9.7 5.9 5.9		80/10200
PLUMS							
Germany, 1973 (Tetzor)	3.2	0.16	4	0 5 7 10 14 21	0.63 0.16 0.15 <0.2 <0.2 <0.2		2221 F73/4A
Germany, 1979 (Hauszwetsche)	2.4	0.16	4	14	1.8 cooked 0.35	0.02 cooked 0.22	22201 F79/15E
Germany, 1976 (Auerbacher)	3.2	0.16	4	0 7 14 21 28	0.17 0.18 0.13 0.10 0.08	<0.01 <0.01 <0.01 <0.01 <0.01	22201 F76/14A

STONE FRUIT Country, year (variety)	Application			PHI, days	Residues, mg/kg		Ref.
	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
Germany, 1976 (Texar)	3.2	0.16	4	0 7 14 21 28	16 2.1 0.40 0.30 <u>0.40</u>	0.06 0.04 0.04 0.03 0.03	22201 F76/15A
Germany, 1979 (Auerbacher)	2.4	0.16	3	14	0.05 cooked 0.03	<0.01 cooked <0.01	22201 F79/13E
Germany, 1979 (Hauszwetche)	2.4	0.16	4	14	2.1 cooked 2.1	<0.01 cooked <0.02	22201 F79/14E

Table 23. Residues in grapes from foliar applications of metiram in supervised trials in Austria, Germany, France, Hungary and Italy. Underlined residues are from treatments according to GAP.

Country, year (variety)	Application				PHI, days	Residues, mg/kg		Ref.
	Form	kg ai/ha	kg ai/hl	No.		EBDC as CS_2	ETU	
Austria, 1982	WP	0.80	0.10	7	57	<u>0.61</u>	0.02	43000 F82/5E
Austria, 1982	WP	0.80	0.10	7	40	0.13	<0.01	43000 F82/3E
Austria, 1982	WP	0.80	0.10	7	40	0.20	<0.01	43000 F82/4E
France, 1980 (Ugni Blanc)	WP	0.32	0.16	11	15	0.14	0.02	43002 F80/2E
France, 1980 (Gamay Beaujolais)	WP	0.32	0.053	7	42	0.15	<0.01	43002 F80/3E
France, 1980 (Aramon)	WP	0.32	0.16	3	39	0.20	0.01	43002 F80/1E
France, 1980 (Pinot Noir)	WP	0.60	0.32	6	76	0.14	<0.01	43002 F80/5E
France, 1980 (Gros Lot)	WP	0.32	0.16	6	42	0.08	0.01	43002 F80/4E
France, 1981 (Grenache Blanc)	WP	1.6-3.2	0.32	13	36	0.14	<0.01	22201 F81/1E
Germany, 1973 (Scheurebe)	WP	3.2	0.16	6	0 5 7 10 14 21 28	2.7 1.0 1.8 1.7 1.6 1.1 1.1		2221 F73/20A
Germany, 1973 (Morio Muskat)	WP	3.2	0.16	6	0 5 7 11 14 21 28	1.7 6.1 3.1 1.0 0.7 0.7 <0.2		2221 F73/22A
Germany, 1973 (Müller Thurgau)	WP	3.2	0.16	9	66	<<u>0.2</u>	0.01	2221 F73/1E
Germany, 1973 (Müller Thurgau)	WP	3.2	0.16	6	0 5 7 10 14 21	2.6 0.33 1.2 1.0 0.7 0.4		2221 F73/21A

PARATHION (058)

EXPLANATION

Parathion was originally evaluated by the JMPR in 1965 and has been reviewed several times since. In 1991 it was extensively re-evaluated and recommendations were made to replace general MRLs for fruits and vegetables by MRLs for specific commodities.

At the 25th Session of the CCPR (1993, ALINORM 93/24A, para 81) the delegation of Germany informed the Committee that the manufacturer would seek re-registration and indicated that a higher MRL for pome fruit was necessary. The proposed MRL was held at step 7B by the 1994 CCPR (ALINORM 95/24, para 150) pending the 1995 JMPR review. At the 27th Session of the CCPR (1995, ALINORM 95/24A, para 103) the manufacturer indicated that additional studies on apples were in progress and would not become available until 1996.

The 1994 CCPR (ALINORM 95/24, para 149) decided to request the JMPR to reconsider the limit of determination of parathion. It also decided to advance the proposals for cotton seed, maize, sorghum, soya bean and sunflower seed to Step 7C to await further information from the USA on registered uses.

Information was provided to the Meeting by the manufacturer on the current use patterns in the USA, supervised trials on cereals and canola, processing trials, freezer storage stability studies and validation of analytical method. Australia, The Netherlands and Peru provided information on current use patterns and data on monitoring.

The current review was scheduled to deal with the commodities held at Step 7B or 7C: apple, cotton seed, maize, sorghum, soya bean (dry) and sunflower seed. The Meeting was aware of a pending review of parathion in the EU and that residue trials were under way in Europe. The Meeting reviewed only those studies that included the commodities at Step 7, analytical methods (with reference to the limit of determination), a report on metabolism in plants and recent reports on estimates of dietary intake.

METABOLISM AND ENVIRONMENTAL FATE

Plant metabolism

Wheat plants were treated with two foliar applications of [*phenyl*-^{14}C]parathion at 1.3 kg ai/ha and grain and straw were harvested 7 days after the final application (Sanger, 1993). The composition of the ^{14}C residues in the grain and straw is shown in Table 1; 72% and 82% of the ^{14}C was extractable from straw and grain respectively with aqueous methanol.

Parathion was the major compound in the residue, and constituted 62% of the ^{14}C in the grain. Paraoxon was not detected in the grain and was a minor component of the residue in the straw. When the unextractable fraction from the straw was digested chemically or with enzymes, additional parathion (1.1 mg/kg) and paraoxon (0.99 mg/kg) were released from the lignin fraction. It is possible that the paraoxon was produced from parathion during the digestion procedure.

Table 1. Composition of the residues in wheat grain and straw harvested 7 days after two applications of [*phenyl*-^{14}C]parathion at 1.3 kg ai/ha (Sanger, 1993).

Residue	Grain		Straw	
	^{14}C as parathion, mg/kg	^{14}C as % of ^{14}C in grain	^{14}C as parathion, mg/kg	^{14}C as % of ^{14}C in straw
Total ^{14}C	10.6		126	
Extractable ^{14}C		82		72
Parathion	6.6	62	46	37
Paraoxon			1.2	0.93
4-nitrophenol	0.79	7.4	13	11
Diethyl 4-acetylaminophenyl phosphate			1.0	0.82
4-nitrophenyl-â-D-glucopyranoside	0.041	0.39	0.73	0.58
O-ethyl *p*-nitrophenyl phosphorothioate	0.027	0.25		
Complex anionic polar metabolites	0.47	4.4	14	11

METHODS OF RESIDUE ANALYSIS

Analytical methods

A suitable procedure was presented (Cassidy, 1991) for the regulatory determination of residues of parathion, paraoxon and 4-nitrophenol in a range of substrates. The sample was extracted with aqueous methanol acidified with HCl and the entire mixture refluxed for 30 minutes. The solution was filtered and concentrated, removing the methanol. Saturated sodium chloride was added before extraction with ethyl acetate. The ethyl acetate was concentrated and parathion and paraoxon determined by GLC with an FPD. An aliquot of the ethyl acetate extract was cleaned up on a Florisil Sep-Pak and the 4-nitrophenol residue was determined by HPLC with UV detection at 315 nm. Variations of the method were needed for some substrates. The limit of quantification was 0.05 mg/kg. Recoveries were found to be satisfactory at this and higher concentrations in about 50 substrates including vegetables, fruits, nuts, cereals, processed commodities and feeding-stuffs.

Keller (1992) used the above method in studies of storage stability with an additional clean-up to remove lipids by gel permeation chromatography. The LOD for each compound was 0.05 mg/kg.

A similar method was used for the analysis of canola seed (Kludas, 1993). Analytical recoveries were 81-92% for parathion and 104-116% for paraoxon at fortification levels of 0.05 and 5.0 mg/kg.

Norby (1993a) described a similar method for parathion and paraoxon residues in cereal commodities. Wheat grain, flour, middlings and shorts were extracted with aqueous acetone, and wheat bran, grain dust, straw and forage with methanol, both extractants acidified with HCl. The analysis were completed as above, but with GLC on a capillary column. The method was validated by testing recoveries at 0.02, 0.05, 0.5 and 5 mg/kg, with the results shown in Table 2. Separate analyses of the commodities spiked at 5 mg/kg with parathion or paraoxon alone verified that there was no conversion of one to the other during analysis. The LOD was 0.02 mg/kg.

Norby (1993b) tested the method on canola and its processed commodities. Fortifications at 0.02 mg/kg of canola seed, crude oil, refined oil and canola meal produced unacceptably high recoveries of paraoxon but recoveries at 0.05 mg/kg were acceptable. The LOD for paraoxon was therefore 0.05 mg/kg and that for parathion 0.02 mg/kg. The results are shown in Table 2.

Table 2. Analytical recoveries of parathion and paraoxon in cereal and canola commodities (Norby, 1993a,b).

Commodity	Fortification, mg/kg	Parathion recoveries, %			Paraoxon recoveries, %		
		Range	Mean	n	Range	Mean	n
Wheat grain	0.02, 0.05, 0.50, 5.0	73-112	95	9	90-101	95	9
Wheat straw	0.02, 0.05, 0.50, 5.0	90-108	96	9	92-119	106	9
Wheat forage	0.02, 0.05, 0.50, 5.0	85-111	96	9	93-104	99	9
Wheat bran	0.02, 0.05, 0.50, 5.0	67-99	86	9	87-107	94	9
Wheat flour	0.02, 0.05, 0.50, 5.0	75-113	85	9	95-112	101	9
Wheat middlings [1]	0.02, 0.05, 0.50, 5.0	79-123	93	9	81-119	93	9
Wheat shorts [2]	0.02, 0.05, 0.50, 5.0	85-103	91	9	86-123	104	9
Wheat grain dust	0.02, 0.05, 0.50, 5.0	73-116	85	9	88-115	95	9
Canola seed	0.02	99 108		2	128 130		2
Canola seed	0.05, 0.5, 5.0	79-94	88	7	101-115	109	7
Canola meal	0.02	85 86		2	121 127		2
Canola meal	0.05, 0.5, 5.0	82-95	88	7	100-116	107	7
Canola refined oil	0.02	92 94		2	104 165		2
Canola refined oil	0.05, 0.5, 5.0	74-80	77	7	81-97	89	7
Canola processing waste	0.02	90 94		2	109 114		2
Canola processing waste	0.05, 0.5, 5.0	74-84	79	7	83-103	93	7

[1] middlings: smaller sieving fraction than bran.
[2] shorts: milled fraction of the middlings retained on the larger sieves.

Price (1991) used a method referred to as MKL-006-88-05. Samples are extracted with aqueous methanol and filtered. The methanol is evaporated and the aqueous phase extracted with ethyl acetate. The concentrated ethyl acetate extract is analysed for parathion and paraoxon by GLC with an FPD. An aliquot of the ethyl acetate extract is cleaned up on a Florisil Sep Pak column and nitrophenol is determined by HPLC.

Sparacino (1992) described similar methods, with validation, for residues of parathion and the two metabolites in wheat, sunflower seed oil, wheat straw and wheat flour. Plant samples are extracted with aqueous methanol or acetone acidified with HC1 and the mixture refluxed for 1 hour. After filtration and evaporation of the solvent the residues are extracted with ethyl acetate and parathion and paraoxon determined as before. An aliquot of the ethyl acetate solution is cleaned up on a small Florisil column and the 4-nitrophenol determined by HPLC. The validated LOD for the three compounds was 0.05 mg/kg. For the analysis of sunflower seed oil a solvent partition step with hexane/acetonitrile was needed to separate the residues from the oil. To confirm identification capillary GC-MS was used with selected ion monitoring at m/z = 109, which corresponds to a fragment of 4-nitrophenol and occurs with all three compounds.

Sparacino found that the determination of parathion and 4-nitrophenol residues was generally

straightforward, but the behaviour of paraoxon during GLC was inconsistent. It was necessary to prime the packed columns with paraoxon and plant extracts and to eliminate column voids for satisfactory results. Analytical recoveries from wheat, wheat straw, wheat flour and sunflower seed oil were parathion (0.05-2 mg/kg) 75-165%, mean 95% (n=30); paraoxon (0.05-0.5 mg/kg) 78-185%, mean 120% (n=30); 4-nitrophenol (0.05-2 mg/kg) 63-162%, mean 108% (n=31).

Szorik (1991) tested the proposed regulatory method for interferences from other pesticide residues. Approximately 200 pesticides were checked for their behaviour on GLC, and those that showed a potential for interference were tested through the method with a variety of substrates. Fenthion and chlorpyrifos came through the extraction and clean-up and interfered with the parathion peak, and phosphamidon, chlorpyrifos-methyl and parathion-methyl interfered with the paraoxon peak.

Stability of pesticide residues in stored analytical samples

Keller (1992) determined the stability of parathion, paraoxon and nitrophenol added at 1 mg/kg as a mixture to macerated snap beans, kidney beans and cotton seed and stored in a freezer for 24 months. The results are shown in Table 3. Control samples were stored for the same times as the test samples and fortified on the day of analysis. The test sample results were then corrected for the recoveries obtained with the companion controls. All test and control samples were analysed in duplicate.

Price (1991) used similar methods to determine the stability of parathion, paraoxon and nitrophenol added at 1 mg/kg to macerated almond kernels, apples, clover, oranges, plums, spinach, strawberries, sunflower seed and sweet peppers and stored at approximately -20°C for 24 months. The results are shown in Table 4.

parathion

Table 3. Freezer storage stability of parathion, paraoxon and nitrophenol added at 1 mg/kg to macerated snap beans, kidney beans and cotton seed and stored at approximately -20°C for 24 months (Keller, 1992).

Storage time, days	% remaining								
	SNAP BEANS			KIDNEY BEANS			COTTON SEED		
	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol
0	106	100	90	128	109	113	100	95	105
30	90	97	104	99	103	93	102	102	102
60	89	89	92	105	100	112	97	100	103
90	102	109	107	102	102	126	95	104	95
120	90	74	109	107	100	109	99	95	89
180	98	121	108	84	83	103	108	69	99
360	104	32	104	100	95	112	101	102	102
540	93	26	103	100	99	91	93	104	113
720	91	29	123	94	84	92	102	98	86

Table 4. Freezer storage stability of parathion, paraoxon and nitrophenol added at 1 mg/kg to macerated almond kernels, apples, clover, oranges, plums, spinach, strawberries, sunflower seed and sweet peppers and stored at approximately -20°C for 24 months (Price, 1991).

Storage time, months	% remaining								
	ALMOND KERNELS			APPLES			CLOVER		
	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol
0	95	99	91	101	102	101	95	109	99
1	84	96	108	99	99	95	101	99	109
2	102	87	93	95	91	96	119	108	106
3	88	104	100	96	93	122	103	77	81
4	96	104	95	92	91	98	112	84	103
6	83	88	94	98	88	90	101	84	105
12	90	99	94	89	79	106	98	78	97
18	80	96	104	98	101	97	101	74	120
24	75	90	106	119	106	132	97	75	116
	ORANGES			PLUMS			SPINACH		
	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol
0	104	104	103	107	108	88	117	120	106
1	94	98	109	97	98	90	88	92	100
2	93	94	103	101	102	108	92	86	101
3	101	103	89	98	98	110	93	89	100
4	98	95	100	104	105	105	115	81	98
6	114	102	101	106	100	95	96	76	86
12	99	96	79	114	106	102	108	75	111
18	99	96	97	92	90	81	74	74	102
24	78	70	81	101	89	89	95	60	92
	STRAWBERRIES			SUNFLOWER SEED			SWEET PEPPERS		
	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol	parathion	paraoxon	nitrophenol

parathion

Storage time, months	% remaining								
0	115	112	104	97	90	93	112	105	103
1	98	97	102	98	87	95	89	79	98
2	94	91	98	90	90	102	85	88	90
3	97	97	106	92	86	92	105	94	97
4	101	107	100	99	98	106	98	77	84
6	109	95	93	102	87	98	83	72	95
12	94	86	89	88	82	91	89	56	89
18	98	92	88	104	104	105	113	77	113
24	98	94	87	77	79	92	93	98	110

USE PATTERN

Information provided on the registered uses of parathion in the USA is shown in Table 5. All aerial applications of EC formulation.

Parathion is registered in the USA for use by aerial application only on field crops for the control of alfalfa weevils, aphids, armyworms, beetles, brown wheat mites, caterpillars, crickets, cutworms, European corn borers, grasshoppers, hoppers, leaf miners, Lygus bugs, moths, spider mites, spittlebugs, sunflower moths, thrips and webworms.

Table 5. Registered uses of parathion in the USA. All aerial applications of EC formulation.

Crop			PHI days
	Rate, kg ai/ha	Number	
Alfalfa	0.28-0.84		15[1]
Barley	0.28-0.84		15[1]
Cotton	0.28-1.1		7[2]
Maize	0.28-1.1		12[3]
Rape seed, canola	0.56		28[4]
Sorghum	0.28-1.1		12[3]
Soya bean	0.28-0.85		20[5]
Sunflowers	0.56-1.1	4	30
Sweet corn	0.28-0.84		12
Wheat	0.28-0.84		15[1]

[1] Do not apply within 15 days of harvest, cutting or forage
[2] Do not feed cotton trash to dairy animals or animals being finished for slaughter within 15 days of application
[3] Do not apply within 12 days of harvest, cutting or forage
[4] Do not graze treated fields or feed treated forage, threshing waste or seed screenings to livestock
[5] Do not apply within 20 days of harvest, cutting or forage

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

Estimates of the intake of parathion in the Australian diet were reported by Stenhouse (1992). The estimated daily intakes for diets based on the average energy intake were adult male 0.0097 ì g/kg bw; adult female 0.0121 ì g/kg bw; boy aged 12 0.0138 ì g/kg bw; girl aged 12 0.0149 ì g/kg bw; child aged 2 0.0259 ì g/kg bw; infant aged 9 months 0.0206 ì g/kg bw. These intakes should be compared with the current parathion ADI of 5 ì g/kg bw.

Dejonckheere *et al*. (1993) estimated the dietary intake of parathion in the Belgian diet arising from food commodities of plant origin. For a 60 kg person the average residue in food prepared for consumption gave an estimated intake of 0.198% of the ADI.

Penttilä and Siivinen (1995) evaluated the dietary intake of pesticide residues, including parathion, in Finland. In 1992 the estimated dietary intake of parathion from domestic and imported foods was 0.005 ì g/kg bw. In 1993 only foods produced in Finland were analysed and no parathion residues were detected.

APPRAISAL

Parathion was originally evaluated by the JMPR in 1965 and was extensively re-evaluated in 1991.

At the 25th Session of the CCPR (1993, ALINORM 93/24A, para 81) the delegation of Germany informed the Committee that the manufacturer would seek re-registration and indicated that a higher MRL for pome fruit was necessary. The proposed MRL was held at step 7B by the 1994 CCPR (ALINORM 95/24, para 150) pending the review by the 1995 JMPR. At the 27th Session of the CCPR (1995, ALINORM 95/24A, para 103) the manufacturer indicated that additional studies on apples were in progress and would not become available until 1996.

The 1994 CCPR (ALINORM 95/24, para 149) decided to request the JMPR to reconsider the limits of determination of parathion. It also decided to advance the proposals for cotton seed, maize, sorghum, soya bean and sunflower seed to Step 7C awaiting further information from the USA on registered uses.

Information was provided to the Meeting by the manufacturer on the current use patterns in the USA and on supervised trials on cereals and canola, supported by processing trials, freezer storage stability data and validation of analytical methods. The current review was scheduled to deal with commodities held at Step 7B or 7C: apple, cotton seed, maize, sorghum, soya bean (dry) and sunflower seed. The Meeting reviewed only those studies that included the commodities at Step 7, analytical methods to deal with the question on the limits of determination, a report on plant metabolism and recent reports on estimates of dietary intake.

In a plant metabolism study parathion was the major component of the residue (62% of the ^{14}C) in wheat grain harvested 7 days after the second application of ring-labelled parathion to the plant. Paraoxon was not detected in the grain and 4-nitrophenol comprised 7.4% of the ^{14}C. Parathion, paraoxon and 4-nitrophenol accounted for 37%, 1.2% and 13% of the ^{14}C in the wheat straw respectively. In the straw and grain 72% and 82% respectively of the ^{14}C was extractable with aqueous methanol.

The GLC methods used in the USA to determine residues of parathion and paraoxon in the majority of crops in the 1991 Evaluations had LODs of 0.05 mg/kg for each compound.

Information was provided on a procedure suitable as a regulatory method for determining residues of parathion, paraoxon and 4-nitrophenol in a range of substrates. The sample is extracted with aqueous methanol acidified with HCl, the entire mixture is refluxed for 30 minutes, then filtered

and concentrated, removing the methanol. The residues are extracted into ethyl acetate, the extract is concentrated and the parathion and paraoxon residues determined by GLC with an FPD. An aliquot of the ethyl acetate extract is cleaned up on a Florisil Sep-Pak and the 4-nitrophenol residue determined by HPLC with UV detection at 315 nm. Variations of the method are needed for some substrates. The LOD for each compound was 0.05 mg/kg. Recoveries were found to be satisfactory at this concentration and higher in approximately 50 substrates including vegetables, fruits, nuts, cereals, processed commodities and feeding materials.

A similar procedure for parathion and paraoxon residues in cereal commodities was described in another report. The LOD was 0.02 mg/kg. When the method was applied to canola and its processed commodities the LOD for parathion was 0.02 mg/kg, but that for paraoxon was 0.05 mg/kg.

When additional identification of residues is needed, capillary GC-MS may be used with selected ion monitoring at m/z = 109, which corresponds to a fragment derived from 4-nitrophenol and occurs with parathion, paraoxon and 4-nitrophenol.

The regulatory method was tested for interferences from other potential pesticide residues. Fenthion and chlorpyrifos came through the extraction and clean-up and interfered with the parathion GLC peak. Similarly phosphamidon, chlorpyrifos-methyl and parathion-methyl interfered with the paraoxon peak.

The storage stability of parathion, paraoxon and nitrophenol residues was measured after adding a mixture of 1 mg/kg of each to macerated snap beans, kidney beans, cotton seed, almond kernels, apples, clover, oranges, plums, spinach, strawberries, sunflower seed and sweet peppers and storing in a freezer for 24 months at approximately -20°C. The three compounds were stable under these conditions, but occasionally the amount of paraoxon remaining after long-term storage was less than 70%, particularly in snap beans.

Parathion is registered in the USA only for aerial application to field crops. The use patterns reported in 1995 for alfalfa, cotton, maize, sorghum, soya beans, sunflowers and wheat are essentially the same as those recorded in the 1991 Residue Evaluations. Use patterns for the additional crops barley, rapeseed or canola and sweet corn have now been reported.

Dietary intake studies in Australia, Belgium and Finland showed that the dietary intake of parathion was much less than the current ADI.

REFERENCES

Cassidy, J.E. 1991. Determination of ethyl parathion [EP: O,O diethyl-O-p-nitrophenyl phosphorothioate] and its metabolites (ethyl paraoxon [EPOX: O,O-diethyl-O-p-nitrophenyl phosphate] and p-nitrophenol [PNP: 4-nitrophenol]) in various matrices. JSCF code 1976.0. Jellinek, Schwartz, Connolly & Freshman, Inc. USA. Unpublished.

Dejonckheere, W., Steurbaut, W., Drieghe, S., Verstraeten, R. and Braeckman, H. 1993. Pesticide residues in food commodities of vegetable origin and the total diet in Belgium 1991-1993. University of Gent, Belgium.

Keller, J.F. 1992. Storage stability of ethyl parathion, ethyl paraoxon, and p-nitrophenol in raw agricultural commodities or processed raw agricultural commodities. Project HLA 6012-240. Hazleton Laboratories America, Inc., USA. Unpublished.

Kludas, R.S. 1993. Magnitude of the residue of ethyl parathion insecticide in canola. Study 92145, includes 92145a, 92145b, 92145c, 92145d, 92145e. Pan-Agricultural Laboratories, Inc. USA. Unpublished.

Norby, N.A. 1993a. Validation of analytical methods for ethyl parathion in spring wheat samples. Study 92211 amended report. Pan-Agricultural Laboratories, Inc. USA. Unpublished.

Norby, N.A. 1993b. Validation of analytical methods for ethyl and methyl parathion in canola samples. Study 92192. Pan-Agricultural Laboratories, Inc. USA. Unpublished.

Penttilä, P.-L. and Siivinen, K. 1995. Control and intake of pesticide residues during 1981-1993 in Finland. National Food Administration, Finland.

Price, D. 1991. Storage stability of ethyl parathion and its metabolite residues in various matrices. Project MKL-006-88-05. McKenzie Laboratories, Inc., USA. Unpublished.

Sanger, T.R. 1993. Ethyl parathion: nature of the residue in wheat. Supplement no. 2 to final report (MRID #407516-01). Project HLA 6222-106. Hazleton Wisconsin, USA. Unpublished.

Sparacino, C.M. 1992. Method validation/confirmation - ethyl parathion and products in plant materials. Project 70C-4996-001. Research Triangle Institute. USA. Unpublished.

Stenhouse, F. 1992. The 1992 Australian Market Basket Survey. National Food Authority. Australian Government Publishing Service, Canberra, Australia.

Szorik, M.M. 1991. Method specificity of the proposed enforcement method used for the determination of ethyl parathion (EP), ethyl paraoxon (EPOX), and p-nitrophenol (PNP) in various matrices. Project 6012-258. Hazleton Wisconsin, USA. Unpublished.

PENCONAZOLE (182)

EXPLANATION

Penconazole was first evaluated in 1992. At the 1994 CCPR the delegation of Germany informed the Committee that German GAP for grapes and pome fruits had changed, requiring a different interpretation of the figures presented in the 1992 JMPR evaluation. New residue data supported a maximum residue level in pome fruits of 0.5 mg/kg instead of the proposed MRL of 0.2 mg/kg. The delegation of France requested clarification of GAP for cucumbers, strawberries and tomatoes with respect to glasshouse and field applications.

The 1992 JMPR requested processing studies on apples and tomatoes, and the determination of residues of penconazole and its metabolites containing the 2,4-dichlorophenyl moiety in field-grown apples and grapes.

The Meeting received updated information on GAP, reports of 33 additional residue trials on pome fruits (apples and pears), 46 trials on grapes, a new analytical method, a freezer storage stability study, and an overall assessment of the residue situation with respect to pome fruits and grapes by the manufacturer (Altenburger, 1995a). Summarized information on GAP for pome fruits, residue data and detailed comments were provided by Germany (Anon., 1994a), information on GAP by Australia, New Zealand and the UK (Anon., 1994c; 1995a,b) and on GAP, analytical methods, residue trials and national MRLs by The Netherlands (Anon., 1994b). Data on supervised trials on leeks, strawberries, gooseberries, black and red currants received from The Netherlands had already been included in the 1992 evaluation and were not re-evaluated by the present Meeting.

This monograph reviews the recent residue data and information on GAP for pome fruits and grapes which were not available to the 1992 JMPR.

METHODS OF RESIDUE ANALYSIS

In addition to the analytical methods described in the 1992 evaluation a method for total residues has been used for analysis in some of the supplied residue studies (Bussmann, 1986). The method determines the residues containing the 2,4-dichlorophenyl group as 2,4-dichlorobenzoic acid.

Samples are extracted by refluxing with 20% concentrated ammonium hydroxide/methanol. The organic solvent is evaporated and the residue dissolved in NaOH. Penconazole and its metabolites are converted to 2,4-dichlorobenzoic acid (DCBA) by refluxing this solution with potassium permanganate. After the addition of water DCBA is partitioned into dichloromethane/hexane on a ClinElut column. The eluted organic phase containing DCBA is evaporated and the residue analyzed by HPLC with UV detection using a 3-column switch system. A factor of 1.49 is used to convert DCBA to penconazole. The LOD for plant material except straw was 0.02 mg/kg as DCBA corresponding to 0.03 mg/kg as penconazole, and for straw 0.04 mg/kg as DCBA corresponding to 0.06 mg/kg as penconazole. The overall mean recovery at 0.06 and 0.3 mg/kg fortification levels was 67%.

In a freezer storage stability study by Buettler (1982), untreated samples of apples and grapes were fortified with 5 mg/kg penconazole and kept at -20°C for 16 months. Reasonable stability of the compound was demonstrated by analyses of samples after 1, 3, 6, and 16 months.

USE PATTERN

The manufacturer clarified GAP for indoor and outdoor applications to cucumbers, tomatoes and strawberries. The open field treatment of all crops is authorized, with the exception of the indoor use on cucumbers in Switzerland (Altenburger, 1995b).

World-wide GAP for the use of

penconazole was reported by the 1992 JMPR. The present Meeting received new and updated information on GAP for pome fruits and grapes from New Zealand and Germany. The information on GAP provided by Australia, France, Greece, Italy and the UK is basically the same as in 1992, but more detailed (see Table 1). GAP for pome fruits and grapes in other countries as well as GAP for other crops is given in the 1992 evaluation.

Penconazole is applied to pome fruits and grapes by foliar spray in EC, WP or tablet (TP) formulations alone or in a mixture with other fungicides, especially captan, dithianon, mancozeb and ziram. The PHI depends on local conditions and varies for pome fruits over a range of 14 days in Italy, Germany and the UK to 42 days in Sweden, and for grapes from 6 or 7 days in Taiwan, Portugal and Uruguay to 35 days in Germany after the last application. Up to 10 or even more treatments are possible. The critical GAP is as follows.

Pome fruits: 0.075 kg ai/ha per application for apples and 0.057 for pears with a PHI of 14 days (Italy, Table 1); 0.09 kg ai/ha per application with a PHI of 14 days (South Africa, 1992 JMPR).

Grapes: 0.15 kg ai/ha per application, PHI 30 days (Morocco, 1992 JMPR); 0.045 kg ai/ha per application, PHI 14 days (Italy, Table 1); 0.05 kg ai/ha per application, PHI 14 days (South Africa, 1992 JMPR); 0.03 kg ai/ha per application, PHI 6 days (Taiwan, 1992 JMPR); 0.05 kg ai/ha per application, PHI 35 days (Germany, Table 1).

Table 1. Registered uses of penconazole.

Crop	Country	Form.	Application			PHI, days
			Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
Apple	Australia	100 EC	0.03-0.087	0.002-0.0025	5	14
	France	25 WP	0.025	0.0025	10-15	15
		100 EC	0.025	0.0025	10	15
		75 TB	0.025	0.0025	10	15
	Germany	25 WP[1]	0.038	0.0025	10	28[1]
		100 WP	0.038	0.0025	12	14
	Italy	32 WP	0.025-0.072	0.0032-0.0048	seve-	15
		100 EC	0.025-0.072	0.0032-0.0048	ral	14
		83 TB	0.025-0.057	0.0025-0.0038	2-3	14
		41.7 TB	0.025-0.057	0.0025-0.0038	2-3	14

Crop	Country	Form.	Application			PHI, days
			Rate, kg ai/ha	Spray conc. kg ai/hl	No.	
		15 WP	0.03-0.068	0.0030-0.0045	3-4	14
		25 WP[2]	0.025-0.075	0.0025-0.005	2-3	14
		25 WP	0.032-0.057	0.0032-0.0038	seve-	14
		50 WP	0.032-0.057	0.0032-0.0038	ral	14
		100 WP	0.032-0.057	0.0032-0.0038		14
	Netherlands	12.5 WP	0.013-0.038	0.0013-0.0025	10-14	21
	New Zealand	10 WP	0.05-0.075	0.0025	4-635	
	UK	25 WP[3]	0.03-0.05		10	14
		100 EC	0.03-0.05		10	14
		25 SC[4]	0.03-0.05		10	28
Pear	France	25 WP	0.025	0.0025	10-15	15
	Italy	32 WP	0.025-0.057	0.0025-0.0038	seve-	15
		100 EC	0.025-0.057	0.0025-0.0038	ral	14
		83 TB	0.025-0.057	0.0025-0.0038		14
		41.7 TB	0.025-0.057	0.0025-0.0038		14
		25 WP[2]	0.025-0.048	0.0025-0.0038		14
		25 WP	0.025-0.048	0.0025-0.0032		14
		50 WP	0.025-0.048	0.0025-0.0032		14
		100 WP	0.025-0.048	0.0025-0.0032		14
	Netherlands	12.5 WP	0.013-0.038	0.0013-0.0025	10-14	21
	New Zealand	10 WP	0.05-0.075	0.0025	4-635	
Pome fruits	Germany	25 WP[1]	0.038	0.0025	12	28[1]
Grapes	France	62.3 EC	0.019		3	30
		5 SC	0.017		seve-	30
		4.4 WP[5]	0.017		ral	30
		4.4 WP[5]		1.54	2	30
		100 EC	0.025		10	30
		75 TB	0.025		10	30
	Germany	100 EC	0.025-0.05	0.0025	6	35
	Greece	100 EC	0.025-0.04	0.0025-0.005		30
	Italy	83 TB	0.02-0.025	0.0025	seve-	14
		41.7 TB	0.02-0.025	0.0025	ral	14
		15 WP	0.018-0.03	0.0023-0.003		14
		25 WP	0.02-0.03	0.0025-0.003		14
		100 EC	0.015-0.045	0.0015-0.003		14
	New Zealand	100 EC	0.05	0.0015-0.0025	4 28	

[1] 25 g/kg penconazole, 600 g/kg mancozeb, PHI determined by ETU residues
[2] 25 g/kg penconazole, 675 g/kg ziram
[3] 25 g/kg penconazole, 475 g/kg captan
[4] 25 g/kg penconazole, 250 g/kg dithianon
[5] 4.4 g/kg penconazole, 700 g/kg mancozeb

RESIDUES RESULTING FROM SUPERVISED TRIALS

Pome fruits. In addition to more than 70 trials reported in the 1992 submission, 25 studies on apples and 9 on pears carried out in Germany, Switzerland and the UK were provided by the manufacturer. Penconazole was applied alone or in a mixture with captan, mancozeb, or dithianon. Up to fifteen sprays were applied, mostly at weekly intervals, at rates of 0.02-0.05 kg ai/ha or 0.06 g ai/tree.

The three trials on apples provided by The Netherlands (report nos. 2118/84, 2119/84 and 2366/84) and several of those from Germany (report nos. 2105/81 and 2304/81) were reviewed by the 1992 Meeting but were reported again, in detail with corrections, to the present Meeting.

The application rates of two trials on pears in France and one in Switzerland were reported incorrectly in the 1992 evaluation (report nos. RR 25/87, RR 26/87 and 2247/81) and have been corrected now. The first two trials on applies (report no. 83/1/943) listed in Table 2 on page 721 of the 1992 evaluation were carried out in New Zealand, not Australia. Details of the new residue trials, the corrected versions of those previously reviewed and all German trials according to GAP are given in Tables 2 (apples) and 3 (pears). The underlined residues of the parent compound are from treatments according to GAP.

Table 2. Residues of penconazole in apples, determined as penconazole or as total residues calculated as penconazole.

Country, Year	Application				PHI, days	Residues, mg/kg		Report
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
Germany	WP	14	0.025 (2)	0.0025	0	0.11		2007/80
1980			0.05 (12)		7	0.10		(JMPR 1992)
					10	0.05		
					21	0.03		
1980	WP	14	0.038	0.0025	0	0.16		2008/80
					7	0.10		(JMPR 1992)
					10	0.07		
					14	<u>0.06</u>		
					21	0.06		
1980	WP	14	0.038	0.0075	0	0.05		2105/81
					6	0.02		(JMPR 1992)
					9	0.02		
					13	<u>0.03</u>		
					20	0.02		
1981	WP	14	0.05	0.0025	17	0.11		2027/81 (JMPR 1992)
1981	WP	14	0.037	0.0075	0	0.06		2304/81
					7	0.07		(JMPR 1992)
					10	0.12		
					14	<u>0.08</u>		
					21	0.09		
1981	WP	14	0.05	0.0025	0	0.06		2028/81
					7	0.03		(JMPR 1992)
					10	0.04		

Country, Year	Application				PHI, days	Residues, mg/kg		Report
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
					14	0.03		
					21	0.03		
1981	WP	14	0.037	0.0075	0	0.11		2029/81
					7	0.11		(JMPR 1992)
					10	0.11		
1982	WP	14	0.037	0.0075	0	0.11		2044/82
					6	0.04		(JMPR 1992)
					10	0.04		
					14	0.03		
					21	0.03		
1986	WP	12	0.037	0.007	0		0.13	2170/86
					7		0.19	
					10		0.11	
					14		0.17	
					21		0.08	
1986	WP	12	0.025	0.003	0		0.11	2171/86
					7		0.08	
					10		0.08	
					14		0.06	
					21		0.05	
1986	WP	12	0.037	0.004	0		0.21	2172/86
					7		0.22	
					10		0.19	
					14		0.35	
					21		0.21	
1986	WP	12	0.037	0.007	0		0.25	2173/86
					7		0.33	
					10		0.32	
					14		0.30	
					21		0.16	
1986	WP	12	0.025	0.003	0		0.11	2174/86
					7		0.06	
					10		0.06	
					14		0.05	
					21		0.06	
1986	WP	11	0.037	0.003	0		0.21	2175/86
					7		0.14	
					10		0.14	
					14		0.16	
					21		0.14	
1986	SC	12	0.037	0.007	0		0.07	2184/86
					7		0.05	

Country, Year	Application				PHI, days	Residues, mg/kg		Report
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
					10		<0.05	
					14		0.05	
					21		0.05	
1986	SC	12	0.025	0.003	0		0.05	2185/86
					7		0.05	
					10		0.05	
					14		0.05	
					21		<0.05	
1986	SC	12	0.037	0.004	0		0.13	2186/86
					7		0.17	
					10		0.08	
					14		0.10	
					21		0.08	
1986	SC	11	0.037	0.003	0		0.06	2188/86
					7		0.11	
					10		0.06	
					14		0.09	
					21		<0.05	
1986	WP	12	0.037	0.007	0		0.19	2179/86
					7		0.17	
					10		0.14	
					14		0.08	
					21		0.13	
1986	WP	12	0.025	0.003	0		0.05	2180/86
					7		0.05	
					10		0.05	
					14		0.05	
					21		0.05	
1986	WP	12	0.037	0.004	0		0.27	2181/86
					7		0.13	
					10		0.13	
					14		0.13	
					21		0.10	
1987	WP	12	0.037	0.003	0		0.11	2163/87
					7		0.08	
					10		0.07	
					14		0.06	
					21		0.10	
1987	WP	12	0.037	0.003	0		0.05	2164/87
					7		0.05	
					10		<0.05	
					14		0.05	

Country, Year	Application				PHI, days	Residues, mg/kg		Report
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
					21		<0.05	
1987	WP	12	0.037	0.003	0		0.12	2165/87
					7		0.06	
					10		0.07	
					14		0.08	
					21		0.06	
Netherlands	WP	5	0.019	0.0013	9	0.02		2118/84 (JMPR 1992)
1984	WP	5	0.025	0.0013	15	0.08		2119/84 (JMPR 1992)
	WP	5	0.025	0.0013	15	0.06		2366/84 (JMPR 1992)
Switzerland	WP	14	0.05	0.0025	0	0.04		2009/80
1980					7	0.03		
					10	0.03		
					14	0.03		
					21	0.02		
					28	<0.02		
1981	WP	14	0.05	0.0025	0	0.06		2031/81
					7	0.03		
					10	0.03		
					14	0.02		
					21	0.02		
					28	0.02		
UK, 1990[1]	EC	10	0.063 g/tree (corresp. to approx. 0.025 kg ai/ha)	0.025	15		0.01 (2), 0.02 (8), 0.03 (2)	CSTR/016:3

[1] 6 trials, 3 locations

Table 3. Residues of penconazole in pears, determined as penconazole or as total residues calculated as penconazole.

Country, Year	Application				PHI, days	Residues, mg/kg		Report
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
France	WP	11	0.019	0.023	13	<0.02		RR 25/87 JMPR 1992
1984	WP	15	0.019	0.023	12	0.19		RR 26/87 JMPR 1992
Germany	WP	12	0.037	0.007	0		0.32	2176/86
1986					7		0.25	
					10		0.32	
					14		0.29	
					21		0.22	
1986	WP	12	0.033 (5)	0.005	0		0.17	2177/86
			0.04 (7)		7		0.16	
					10		0.13	
					14		0.06	
					21		0.08	
1986	WP	12	0.037	0.007	0		0.40	2182/86
					7		0.27	
					10		0.14	
					14		0.16	
					21		0.22	
1986	SC	12	0.033 (5)	0.005	0		0.22	2187/86
			0.04 (7)		7		0.11	
					10		0.10	
					14		0.06	
					21		0.07	
1986	SC	12	0.037	0.006	0		0.24	2189/86
					7		0.18	
					10		0.11	
					14		0.15	
					21		0.10	
1987	WP	12	0.037	0.007	0		0.08	2167/87
					7		0.08	
					12		0.07	
					14		0.05	
					21		0.05	
					30		0.05	
1987	WP	12	0.037	0.002	0		0.14	2168/87
					7		0.18	
					10		0.11	
					14		0.12	
					21		0.10	
Switzerland	WP	14	0.025	0.0013	0	0.06		2247/81
1981					3	0.05		JMPR 1992

Country, Year	Application				PHI, days	Residues, mg/kg		Report
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
					7	0.03		
					10	0.03		
					14	0.02		
1986	WP	12	0.025	0.003	0		0.14	2178/86
					7		0.10	
					9		0.10	
					14		0.08	
					21		0.08	
					28		0.05	
1986	WP	12	0.025	0.003	0		0.13	2183/86
					7		0.08	
					9		0.08	
					14		0.08	
					21		0.06	
					28		0.05	

Grapes. In addition to more than 100 residue trials listed in the 1992 evaluation, 46 residue trials on grapes carried out in France, Germany and Switzerland were reported by the manufacturer. Penconazole was applied alone or in a mixture with captan, mancozeb or dithianon. Up to ten sprays were applied, mostly at weekly intervals, at rates between 0.001 and 0.086 kg ai/ha. Residues were determined as parent penconazole, as total residues containing the 2,4-dichlorophenyl moiety, or both.

Details of the new residue trials are given in Table 4. The underlined residues of the parent compound are from treatments according to GAP.

Table 4. Residues of penconazole in grapes, determined as penconazole or as total residues calculated as penconazole.

Country, Year	Application				PHI, days	Residues, mg/kg		Report & notes
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
France, 1981	EC	9	0.014-0.034	0.005	28	0.02		43/82
1981	EC	8	0.020-0.040	0.005	48	<0.02		42/82
1981	EC	9	0.013-0.047	0.005	20	<0.02		41/82
1983	EC	6	0.004-0.012	0.002	51	<0.02		07/84
1984	EC	7	0.001-0.005	0.0005	55	<0.02		61/85
1993	EC	8	0.014-0.016	0.0015	30	<0.02 (2)	0.07 (2)	2072/93
1993	EC	8	0.030-0.033	0.0031	30	<0.02	0.09	2072/93B
1993	TB	8	0.015-0.028	0.0016-0.0028	30	<0.02 (2)	<0.07, 0.07	2072/93C
1993	TB	8	0.03-0.06	0.0032-0.0055	30	<0.02	0.09	2072/93D
1993	EC	8	0.015-0.016	0.0015-0.0016	28	<0.02 (4)	0.07 (4)	2073/93
1993	EC	8	0.03-0.032	0.0031	28	<0.02	0.14	2073/93B
1993	EC	8	0.015	0.0015	30	0.04, 0.03	0.24, 0.17	2074/93
1993	EC	8	0.028-0.031	0.0031	30	0.08	0.47	2074/93B
1993	TB	8	0.015-0.016	0.0016	30	0.04, 0.03	0.19, 0.20	2074/93C

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Country, Year	Application				PHI, days	Residues, mg/kg		Report & notes
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
1993	TB	8	0.030-0.032	0.0016	30	0.07	0.38	2074/93D
1993	EC	8	0.015-0.016	0.0015	30	<0.02 (4)	0.06(2), 0.07, 0.08	2075/93
1993	EC	8	0.030-0.031	0.0031	30	<0.02	0.14	2075/93B
Germany	WG	6	0.009 (1)	0.003-0.004	0		0.06	2186/87
1987			0.012 (1)		14		0.10	
			0.018 (1)		28		0.08	
			0.024 (2)		35		0.07	
			0.03 (1)		42		0.10	
1987	WG	6	0.009, 0.012,	0.002	0		0.12	2187/87
			0.024, 0.028,		14		0.05	
			0.031, 0.036		28		0.05	
					35		0.05	
					42		<0.05	
1987	WG	6	0.015, 0.018,	0.002-0.003	0		0.30	2188/87
			0.022 (2),		14		0.21	
			0.03 (2)		28		0.16	
					35		0.21	
1987	WG	6	0.012	0.005	0		0.05	2189/87
			0.015		14		<0.05	
			0.018		28		0.10	
			0.024		35		0.08	
			0.026 (2)		42		0.05	
1987	WG	6	0.006	0.003-0.007	0		0.61	2190/87
			0.01		7		0.60	
			0.015		14		0.52	
			0.02		21		0.30	
			0.028 (2)		28		0.39	
					35		0.43	
1988	EC	6	0.016 (2)	0.003-0.006	0	0.04		CGD 67/88
			0.024 (2)		14	0.02		
			0.027		28	0.05		
			0.031		35	0.04		
					42	0.02		
1988	EC	6	0.016 (2)	0.003-0.006	0	0.01		CGD 68/88
			0.024 (2)		14	0.02		
			0.027		28	0.04		
			0.031		35	0.02		
					42	0.03		
1988	EC	6	0.009, 0.012,	0.0015	0	<0.02		CGD 69/88
			0.018, 0.021,		14	<0.02		last treatment
			0.024, 0.027		28	<0.02		at stage 33-35
					35	<0.02		
					42	<0.02		
1988	EC	6	0.009	0.0015	0	0.04		CGD 70/88

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Country, Year	Application				PHI, days	Residues, mg/kg		Report & notes
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
			0.012		14	<0.02		last treatment
			0.018		28	<0.02		at stage 33-35
			0.021		35	<0.02		
			0.024		42	<0.02		
			0.027					
1988	EC	6	0.024 (2)	0.0015-0.0023	0	0.17		CGD 71/88
			0.029 (2)		14	0.02		last treatment
			0.036 (2)		28	0.04		at stage 35
					35	<0.02		
					42	0.08		
1988	EC	6	0.024 (2)	0.0015-	0	0.11		CGD 72/88
			0.029 (2)	0.0023	14	0.04		last treatment
			0.036 (2)		28	0.03		at stage 35
					35	0.04		
					42	0.05		
Italy,	EC	8	0.05	0.003	0	0.34		2314/84
1984					7	0.21		
					15	0.07		
					22	0.12		
1984	EC	6	0.02-	0.003	0	0.08		2315/84
			0.03		8	0.09		
					14	0.06		
					22	0.02		
1992	EC	7	0.023	0.003	9	<0.02		2086/92
					23	0.18		
					36	<0.02		
					43	<0.02		
					50	<0.02		
1992	EC	5	0.032	0.003	0	0.05		2087/92
					14	<0.02		
					28	<0.02		
					37	<0.02		
					45	<0.02		
1993	EC	10	0.032-0.033	0.002	14	0.05(2),	0.23, 0.25,	2076/93
						0.06, 0.07	0.28, 0.32	
1993	EC	10	0.064-0.066	0.0041	14	0.10	0.48	2076/93B
1993	EC	10	0.032-0.033	0.002	14	0.02 (2)	0.16, 0.17	2077/93
1993	EC	10	0.063-0.066	0.0041	14	0.06	0.33	2077/93B
1993	TB	10	0.020 (9), 0.042	0.0013-0.0026	14	<0.02 (2)	0.10, 0.11	2077/93C
1993	TB	10	0.042 (9), 0.084	0.0026-0.0052	14	0.02	0.16	2077/93D
1993	EC	10	0.032-0.033	0.002	14	0.03, 0.04	0.15, 0.21	2078/93
1993	EC	10	0.065-0.067	0.0041	14	0.06	0.27	2078/93B
1993	TB	10	0.021 (9), 0.042 (1)	0.0013-0.0026	14	<0.02, 0.02	0.08, 0.09	2078/93C

Country, Year	Application				PHI, days	Residues, mg/kg		Report & notes
	Form.	No.	kg, ai/ha	kg, ai/hl		Parent	DCBA	
1993	TB	10	0.042 (9), 0.084 (1)	0.0026-0.0052	14	0.03	0.20	2078/93D
South Africa	EC	1	0.03	0.003	0		0.16	2330/87
					3		0.14	
1988					7		0.10	
					14		0.08	
					21		0.12	
1988	EC	1	0.045	0.005	0		0.22	2331/87
					3		0.21	
					7		0.14	
					14		0.14	
					21		0.18	
1988	EC	1	0.03	0.003	0		0.28	2332/87
					3		0.22	
					7		0.22	
					14		0.14	
					21		0.12	
Switzer-	EC	6	0.065-	0.005	0	0.09		2023/80
land,			0.11		7	0.03		
1981					14	0.02		
					21	<0.02		
					35	<0.02		
					42	<0.02		
					49	<0.02		
					56	<0.02		

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were received.

In processing

Grapes. Grapes from selected residue trials were processed to wine (new), wine (6-month old), juice, must, raisins, raisin waste, and wet and dry pomace (Table 5). The field treatments and application rates are shown in Table 4.

Table 5. Residues of penconazole in processed products of grapes.

Country, Year	Sample	Days after last appl.	Residues, mg/kg		Report
			parent	DCBA	
France	grapes	28	0.02		43/82
1981	wine		<0.01		
1981	grapes	48	<0.02		42/82
	wine		<0.01		
1981	grapes	20	<0.02		41/82
	wine		<0.01		
1983	grapes	51	<0.02		07/84
	wine		<0.01		
1984	grapes	55	<0.02		61/85
	wine		<0.01	1993	
1993	grapes	28	<0.02	0.07	2073/93
	grapes before processing		<0.02	0.07	
	raisins		<0.02	0.14	
	raisin waste		0.03	0.25	
	wet pomace		<0.02	<0.2	
	dry pomace		0.04	0.41	
	juice		<0.02	0.08	
	must		<0.02	<0.06	
	wine, new		<0.02	<0.06	
	wine, 6 month		<0.02	<0.06	
1993	grapes	28	<0.02	0.14	2073/93B
	grapes before processing		<0.02	0.15	
	raisins		0.02	0.38	
	raisin waste		0.05	0.58	
	wet pomace		0.04	0.31	
	dry pomace		0.11	1.2	
	juice		<0.02	0.09	
	must		<0.02	0.06	
	wine, new		<0.02	<0.06	
	wine, 6 month		<0.02	<0.06	
1993	grapes	30	<0.02	0.06, 0.08	2075/93
	raisins		0.02	0.23	
	raisin waste		0.04	0.57	
	wet pomace		0.03	0.20	
	dry pomace		0.05	0.33	
	juice		<0.02	<0.07	
	must		<0.02	<0.07	
	wine, new		<0.02	0.06	
	wine, 6 month		<0.02	<0.06	

Country, Year	Sample	Days after last appl.	Residues, mg/kg		Report
			parent	DCBA	
1993	grapes	30	<0.02	0.13, 0.14	2075/93B
	raisins		0.03	0.77	
	raisin waste		0.04	1.0	
	wet pomace		0.06	0.42	
	dry pomace		0.10	0.58	
	juice		<0.02	0.07	
	must		<0.02	0.07	
	wine, new		<0.02	0.10	
	wine, 6 month		<0.02	0.10	
Germany	grapes	42	0.02		CGD 67/88
1988	must		0.01		
	wine		<0.01		
1988	grapes	42	0.03		CGD 68/88
	must		<0.01		
	wine		<0.01		
1988	grapes	42	<0.02		CGD 69/88
	must		<0.01		
	wine		<0.01		
1988	grapes	42	<0.02		CGD 70/88
	must		<0.01		
	wine		<0.01		
1988	grapes	42	0.08		CGD 71/88
	must		<0.01		
	wine		<0.01		
1988	grapes	42	0.05		CGD 72/88
	must		<0.01		
	wine		<0.01		
Italy	grapes	14	0.05, 0.07	0.23, 0.32	2076/93
1993	grapes before processing		0.05	0.24	
	raisins		0.11	0.87	
	raisin waste		0.21	1.4	
	wet pomace		0.26	0.83	
	dry pomace		1.1	2.5	
	juice		<0.02	0.09	
	must		<0.02	0.07	
	wine, new		<0.02	0.11	
	wine, 6 month		<0.02	0.14	
1993	grapes	14	0.10	0.48	2076/93B
	grapes before processing		0.08	0.34	
	raisins		0.32	2.9	

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Country, Year	Sample	Days after last appl.	Residues, mg/kg		Report
			parent	DCBA	
	raisin waste		0.57	3.1	
	wet pomace		0.60	1.9	
	dry pomace		2.1	5.3	
	juice		<0.02	0.16	
	must		<0.02	0.13	
	wine, new		<0.02	0.30	
	wine, 6 month		<0.02	0.27	

NATIONAL MAXIMUM RESIDUE LIMITS

The manufacturer reported new Belgium MRLs of 0.2 mg/kg for small seed fruit such as pome fruit and for grapes. Australia extended the MRL of 0.1 mg/kg for apples (JMPR 1992) to pome fruit. For the other commodities see the 1992 evaluation.

APPRAISAL

Penconazole is a systemic triazole fungicide first evaluated in 1992.

At the 1994 CCPR the delegation of Germany stated that German GAP for grapes and pome fruits had been changed, and questioned the interpretation by the JMPR of the figures presented in the 1992 evaluation. The delegation of France requested clarification of the GAP for cucumbers, strawberries and tomatoes with respect to glasshouse and field applications.

The 1992 JMPR requested processing studies on apples and tomatoes and a method for the determination of residues of penconazole and its metabolites containing the 2,4-dichlorophenyl moiety in field-grown apples and grapes, because residues of the parent compound were found in metabolism studies on apples and grapes at only 10-15 % of the total residue levels.

The Meeting received updated information on GAP, the results of additional residue trials on pome fruits and grapes, a new analytical method, a study of freezer storage stability and an overall assessment of the residue situation for pome fruits and grapes by the manufacturer. Information on GAP for pome fruits, residue data and detailed comments were provided by Germany, and information on GAP by Australia, The Netherlands, New Zealand and the UK. Analytical methods, residue data and national MRLs were also provided by The Netherlands.

In addition to the analytical methods described in the 1992 evaluation a method for determining total residues of penconazole and all metabolites containing the 2,4-dichlorobenzyl group as 2,4-dichlorobenzoic acid (DCBA) has been used in some of the trials. Determination is by HPLC with UV detection. The LOD for plant material except straw was 0.02 mg/kg as DCBA corresponding to 0.03 mg/kg calculated as penconazole, and for straw 0.04 mg/kg as DCBA corresponding to 0.06 mg/kg as penconazole. The overall mean recovery at 0.06 and 0.3 mg/kg fortification levels was 67%.

Penconazole was stable for at least 16 months in apples and grapes under frozen conditions.

The Meeting was informed that GAP for cucumbers, tomatoes and strawberries refers to field treatments but the indoor use of penconazole on cucumbers is authorized in Switzerland.

GAP for the world-wide use of penconazole on all commodities was reported by the 1992 JMPR. The Meeting received updated information on GAP for pome fruits and grapes from Germany. The information on GAP provided by Australia, France, Greece, Italy and the UK was basically the same as in 1992.

Penconazole is applied to pome fruits and grapes by foliar spray as EC, WP or tablet (TP) formulations, alone or mixed with other fungicides. Up to 10 or more spray treatments with maximum rates of 0.07 kg ai/ha (Italy) or 0.09 and 0.15 kg ai/ha (South Africa, Morocco) are allowed.

The present Meeting reviewed the new residue data on pome fruits and grapes in the context of previous reviews.

Pome fruits. The 1992 JMPR estimated a maximum residue level of 0.2 mg/kg for pome fruits, based on numerous European trials with residues generally below 0.1 mg/kg, but also up to 0.17 mg/kg.

In addition to the trials evaluated in 1992, the present Meeting received reports of twelve German residue trials on apples and seven on pears from 1986-87 which accorded with German GAP (10-12 treatments with 0.038 kg ai/ha, 14-day PHI), but total residues were determined instead of those of the parent compound. Although the PHI for pears is 28 days (because a mixed formulation with mancozeb is used and the PHI is determined by ETU residues from mancozeb) the Meeting considered the 14-day residues on pears because the residue behaviour on apples and pears is comparable. Penconazole was applied 11 or 12 times at 0.037 kg ai/ha. After 14 days the total residues in apples ranged from 0.05 to 0.35 mg/kg and in pears from 0.05 to 0.29 mg/kg. As the residue is defined as penconazole the total residues were not used in estimating a maximum residue level, but were noted as useful additional information. The Meeting agreed to maintain the current recommendation of 0.2 mg/kg for pome fruits.

Grapes. The 1992 JMPR estimated a maximum residue level of 0.2 mg/kg for penconazole in grapes, based on a large number of trials with residues generally below 0.2 mg/kg four weeks after the last treatment.

The present Meeting received data from numerous new trials according to GAP. In French trials in 1993 penconazole was applied eight times a season at rates from 0.014 to 0.028 kg ai/ha. Residues at PHIs of 28-30 days ranged from <0.02 to 0.04 mg/kg for the parent, and from <0.07 to 0.24 mg/kg for total residues. In three trials in South Africa (1 treatment, 0.03-0.045 kg ai/ha) total residues 14 days after the last treatment were from 0.08 to 0.14 mg/kg. Eleven German trials (6 treatments with 0.006-0.036 kg ai/ha) showed maximum total residues of 0.43 mg/kg and parent residues of 0.04 mg/kg (35-day PHI) and ten Italian trials (5-10 treatments with 0.002-0.003 kg ai/hl, 0.02-0.08 kg ai/ha) gave total residues from 0.1 to 0.32 mg/kg and parent residues from <0.02 to 0.07 mg/kg at a 14-day PHI.

Because the parent penconazole is the relevant residue with regard to consumer safety, the total residues determined as DCBA were not used for the estimation of a maximum residue level. The Meeting agreed to maintain the current recommendation of 0.2 mg/kg for grapes.

Raisins and grape pomace. Processing studies were carried out on grapes. Although parent residues were not detectable in wine and juice, they were found in raisins and wet pomace. Residues of the parent compound in 2 Italian trials were concentrated in raisins and dry pomace by factors of 2-3 and 22 respectively. Total residues as DCBA in 6 trials showed concentration factors ranging from 2 to 6 for raisins and from 4.5 to 11 for dry pomace. The Meeting estimated a maximum residue level of 0.5 mg/kg for dried grapes (raisins).

RECOMMENDATIONS

The Meeting estimated the maximum residue level shown below for dried grapes (i.e. currants, raisins and sultanas) which is recommended for use as an MRL.

Definition of the residue: penconazole

Commodity		Recommended limit, mg/kg		PHI on which based, days
CCN	Name	New	Previous	

DF 0269	Dried grapes (currants, raisins and sultanas)	0.5	-	30[1]

[1] PHI for fresh grapes

FURTHER WORK OR INFORMATION

Desirable

Processing studies on apples and tomatoes (from 1992).

REFERENCES

Altenburger, E. 1995a. Penconazole - Second Working Paper prepared by Ciba-Geigy Ltd., Basel, Switzerland, March 1995. Unpublished.

Altenburger, E. 1995b. Penconazole (CGA 71818) - JMPR 1995. Letter from Ciba-Geigy Ltd., Basle, 08. June 1995. Unpublished.

Anon. 1994a. Information on GAP, residue data and explanatory notes on Penconazole for the 1995 JMPR. Federal Biological Research Centre for Agriculture and Forestry, Federal Republic of Germany, May, 1994. Unpublished.

Anon. 1994b. Information from The Netherlands on pesticides to be considered by the JMPR 1995 - penconazole. Ministrie van Volksgezondheid, Welzijn en Sport, Netherlands, August, 1994. Unpublished.

Anon. 1994c. Information on GAP for penconazole for the 1995 JMPR by Pesticides Safety Directorate, UK. Unpublished.

Anon. 1995a. Information on GAP and national MRLs for penconazole for the 1995 JMPR by Agricultural and Veterinary Chemicals Policy Section of Department of Primary Industries and Energy, Australia, April 12, 1995. Unpublished.

Anon. 1995b. Information on GAP for penconazole for the 1995 JMPR. Ministry of Agriculture and Fisheries, New Zealand, May 25, 1995. Unpublished.

Buettler, B. 1982. CGA 71818, Deep freeze stability of residues in apples and grapes; Ciba-Geigy Ltd., Basel, Switzerland, Rep.-No. SPR 17/82, 05.05.1982. Unpublished.

Bussmann, W. 1986. Analytical method REM 11/86: Penconazole (CGA-71818) determination of total residues as 2,4-dichlorobenzoic acid by liquid chromatography - plant material. Ciba-Geigy Ltd., Basel, Switzerland, 02.09.1986. Unpublished.

JMPR, 1992. Pesticides residues in food. Evaluations 1992, Part I - Residues. FAO Plant Production and Protection Paper 118, FAO, Rome, 1993.

PROFENOFOS (171)

EXPLANATION

Profenofos was first evaluated by the 1990 JMPR which estimated several temporary maximum residue levels, some of which were revised or withdrawn in 1992. The 1994 JMPR recommended new limits for common beans and chilli peppers, confirmed several recommendations for MRLs, withdrew the recommendation for onions and removed the temporary restriction from others.

At the 1995 CCPR the GAP basis for the 1992 JMPR recommendations for head cabbage and cotton seed, and the limit of determination for meat were questioned. The CCPR held the MRLs for these commodities at Step 7B. The draft MRL for tea was held at step 6 pending clarification of the GAP PHI. The Meeting received clarification of GAP for tea and information from Germany regarding the question on cotton seed. The Meeting reviewed the new information and considered the questions on meat and head cabbage on the basis of the information in the earlier monographs.

RESIDUES RESULTING FROM SUPERVISED TRIALS

Cotton seed. At the 1995 CCPR a delegation objected that the maximum residue level of 3 mg/kg estimated by the 1992 JMPR for cotton seed had been based on exaggerated application rates. The 1990 JMPR had initially estimated a temporary level of 1 mg/kg, based on a 21-day PHI, pending the receipt of information on GAP. Substantial information on GAP provided to the 1992 JMPR led that Meeting to recommend an increase to 3 mg/kg, based on the more common 14-day PHI and the residue data reviewed in 1990. The limited additional data reviewed by the 1994 JMPR (residues were <0.03 mg/kg) did not require a change.

Documentation provided to the present Meeting by the German government (Evers, 1995) showed that some of the residues in the US trials recorded in Reports 3928-A and 3963 of the 1990 monograph had erroneously been reported as resulting from 1.1 kg ai/ha, when in fact the rate was 2.2 kg ai/ha (twice the GAP rate). It was some of these residues (1.8, 2.8 mg/kg after 14 days, 2.6, 2.1 mg/kg after 21 days and 2.3, 2.2 mg/kg after 30 days) that prompted the 1992 JMPR to recommend the increase from 1 to 3 mg/kg. Those residues which were correctly recorded in the 1990 monograph as resulting from GAP application rates of 1-1.1 kg ai/ha at PHIs of ≥14 days (the Australian GAP PHI is 28 days and the US 14 days) are shown in Table 1, where the underlined residues are at GAP PHIs.

Table 1. Residues resulting from the use of profenofos on cotton seed in Australia and the USA at 1-1.1 kg ai/ha (from 1990 monograph, Table 12 corrected).

Country/No. of trials	Residues, mg/kg, at PHI (days)			
	14-15	21	28-30	36
Australia				
trial 2	1.2[1]		<u>0.65</u>[1]	
trial 3	0.8	0.23	<u>0.1</u>	0.05, 0.04
trial 4	0.1	0.07	<u>0.03</u>	
USA				
trial 1	<u>0.08</u>	0.25		
trial 2[2]	<u>1, 0.93</u>	0.47, 0.46	0.23, 0.26	
trial 3[2]	<u>0.8, 1.1</u>	1, 1.2		

[1] Mean of 4 analyses

[2] Reports 3928-A (trial 2) and 3963 (trial 3) do not indicate whether the two values are from duplicate analyses or duplicate samples.

Meat. The 27th CCPR held the recommended MRL for meat of 0.02 mg/kg (at the limit of determination) at Step 7B pending clarification of the limit of determination for meat. The recommendations of the 1990 JMPR for meat, milks and eggs were confirmed by the 1992 JMPR. Pages 369 and 372 of the 1990 JMPR monograph state that the limit of determination for meat is 0.05 mg/kg, so the recommendation of an MRL of 0.02 mg/kg was an error.

Tea. A temporary maximum residue level for tea of 0.5 mg/kg estimated by the 1990 JMPR was based on a 21-day PHI and an application rate of 1 kg ai/ha in Japanese trials. It was temporary pending information on Japanese GAP. The information on Japanese GAP provided to the 1992 JMPR (40 g ai/hl) could not be compared to the kg ai/ha rate of the trials, so the temporary restriction was retained. Since information provided to the 1994 JMPR confirmed that the application rate used in the trials was according to GAP, that Meeting confirmed the 0.5 mg/kg estimate and recommended that it should no longer be temporary.

At the 27th (1995) CCPR a question arose concerning the GAP PHI. The proposed MRL had been based on a 21-day PHI, which was recorded in the 1990 monograph (page 371) as Japanese GAP. The Meeting received confirmation that a 21-day PHI had in fact been GAP in Japan, but the label recommendation had since been revised (Altenburger, 1995). The current recommendation is for application after the last plucking, making it in effect a post-harvest application. However, although recommending application after the last plucking, the label recognizes that applications before harvest may be needed, especially for the less common autumn/winter harvest. A 30-day PHI is recommended to accommodate that need, primarily to minimize an odour problem.

APPRAISAL

Profenofos was reviewed by the JMPR in 1990, 1992 and 1994. At the 1995 CCPR questions were raised concerning the basis for the limits recommended for cotton seed and meat, which were held at Step 7B, and for tea which was held at step 6. The Meeting reviewed additional information provided for cotton seed and tea and considered the question on meat on the basis of information in earlier JMPR monographs. The Meeting also considered information provided to clarify GAP for green peppers in the context of data evaluated by the 1994 JMPR.

Cotton seed. The Meeting received confirmation that residues up to 2.8 mg/kg after 14 days reported in 1990 had been erroneously recorded as being from GAP treatments, whereas in fact the applications had been at twice the GAP rate. The original reports show that maximum residues after 14 days from the GAP application rate were $\leq$1.2 mg/kg. The Meeting noted that several results from a relatively limited number of trials were very close to or slightly above 1 mg/kg, concluded that although a 3 mg/kg limit was not required, a 1 mg/kg limit might be too low, and recommended reduction of the 3 mg/kg proposal to 2 mg/kg. The Meeting saw no need to revise the current proposal of 0.05 mg/kg (at the limit of determination) for edible cotton seed oil.

Meat. The Meeting re-examined the text of the 1990 JMPR monograph to resolve the question raised at the 1995 CCPR, on the limit of determination for profenofos in meat. The recommendation recorded in 1990 is 0.02* mg/kg, but the 1990 monograph makes it clear that the limit of determination in meat is 0.05 mg/kg. The Meeting concluded that 0.02 mg/kg had been recorded in error and recommended that the estimate of 0.02 mg/kg should be changed to 0.05 mg/kg.

Teas (tea and herb teas). The 1994 JMPR had confirmed the temporary maximum residue level of 0.5 mg/kg estimated by the 1990 JMPR for tea. The 21-day PHI used for the estimate was questioned at the 1995 CCPR. The Meeting was informed that the GAP PHI had since been revised to 30 days. Because the available data no longer accorded with GAP the Meeting recommended withdrawal of the previous estimate.

Peppers, Sweet. The 1994 JMPR concluded that the available data on green peppers could support an estimate of a maximum residue level of 0.5 mg/kg after 28 days if the application rates of 0.2-0.65 kg ai/ha used in the trials could be related to Italian GAP. Information provided to the present Meeting confirmed that the applications were equivalent to 0.04 to 0.05 kg ai/hl, which is the concentration specified in Italian GAP (one application at 0.04-0.05 kg ai/hl, equivalent to 0.24-0.4 kg ai/ha, with a 28 day PHI). With this confirmation that GAP had been followed and the observation that even at exaggerated rates residues only slightly exceeded 0.5 mg/kg the Meeting endorsed the 1994 JMPR view and estimated a maximum residue level of 0.5 mg/kg.

RECOMMENDATIONS

The Meeting recommended the changes shown in the Table below.

Definition of the residue: profenofos.

Commodity		Recommended MRL (mg/kg)		PHI (days)
CNN	Name	New	Previous	
SO 0691	Cotton seed	2	3	14
MM 0095	Meat	0.05*	0.02*	--
VO 0045	Peppers, sweet	0.5	--	28
DT 0171	Teas (Tea and Herb Teas)	W[1]	0.5	21

* At or about the limit of determination
[1] Withdrawn

REFERENCES

Altenburger, E., 1995. Letter to F. Ives, June 8, 1995 and attachment "PHI of Profenofos (Encedan) in tea in Japan" (M. Sasaki, Ciba Japan, June 2, 1995).

Evers. 1995. Letter to B. Murray, May 23, 1995 and attachments, including Reports 3928-A and 3963.

QUINTOZENE (064)

EXPLANATION

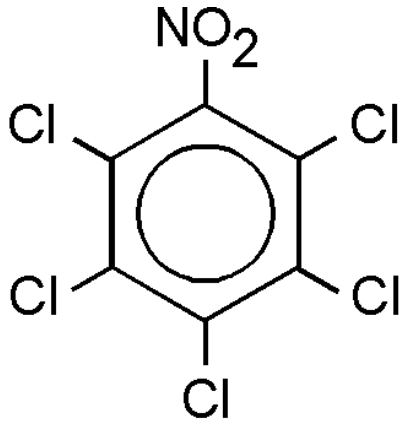
Quintozene, originally evaluated by the JMPR in 1969 and re-evaluated for residues several times up to 1977, is included in the CCPR periodic review programme as the ADI was established before 1976 (ALINORM 89/24A, para 298 and Appendix V). The 1991 CCPR scheduled the periodic review for the 1995 JMPR as the manufacturer had reported that new data would be available (ALINORM 91/24A, para 316 and Appendix VI para 15).

The Meeting received animal and plant metabolism studies, information on analytical methods and updated GAP, supervised residue trials on vegetables and oilseed, and information on residues after storage and processing from the manufacturer (Gaydosh, 1995a). Information on analytical methods and national MRLs was supplied by The Netherlands (Anon., 1994a) and on GAP by Australia (Anon., 1995a), Canada and the UK (Anon., 1995b; 1994b). Germany and The Netherlands informed the Meeting that there were no registered uses in their countries.

IDENTITY

Iso common name: quintozene
Chemical name
IUPAC and CA: pentachloronitrobenzene
CAS No: 82-68-8
CIPAC No: 78
Synonyms: PCNB

Structural formula:



quintozene

Molecular formula: $C_6Cl_5NO_2$
Molecular weight: 295.34

Physical and chemical properties

Pure active ingredient and technical material[1]

Vapour pressure: 9.5×10^{-5} mm HG at 25°C (Thomson, 1989), corresponding 1.27×10^{-2} Pa at 25°C
Melting point: 142-145°C
Boiling point: 328°C (760 mm HG)
Octanol/water partition coefficient: 10^5-10^6 (Polakoff, 1987)
Solubility:

Acetonitrile	70 g/kg
Cyclohexane	70 g/kg
Ethanol	20 g/kg
Ethyl acetate	210 g/kg
Heptane	30 g/kg
Methanol	20 g/kg
Toluene	1400 g/kg
Water	1×10^{-6} g/l at 25°C (Batorewicz, 1988)

Specific gravity: 1.718 at 25°C
Hydrolysis: no hydrolysis in the pH range 5-7 (Bowman, 1988)
Purity: >99%

Hexachlorobenzene content

Hexachlorobenzene (HCB) occurs as an impurity in the manufacture of quintozene. Before 1988, the

[1] The current technical material is >99% pure, so the "pure active ingredient" and "technical material" are effectively the same

HCB content of the technical material was approximately 0.5%. In 1988 modifications to the manufacturing process reduced the level of HCB to 0.1% or less.

The marketing and use in plant protection products of quintozene containing more than 1 g/kg of HCB or more than 10 g/kg pentachlorobenzene (PB) is prohibited in the European Union (Anon., 1990).

Formulations

Emulsifiable concentrate (EC)
Dustable powder (DP)
Flowable concentrate for seed treatment (FS)
Granule (GR)
Solution for seed treatment (LS)
Seed coated with a pesticide (PS)
Suspension concentrate (flowable concentrate, SC)
Wettable powder (WP)

METABOLISM AND ENVIRONMENTAL FATE

Animal metabolism

Metabolism of quintozene was investigated in rats, goats and chickens. The biochemical pathways of quintozene in all these species were found to be nearly the same. The major routes were (1) displacement of nitro group by (a) the sulfhydryl group of reduced glutathione or of an SH-containing amino acid or peptide, or (b) a hydroxyl group to yield pentachlorophenol; (2) reduction of the nitro group to form *N*-pentachlorophenylhydroxylamine, pentachloroaniline and conjugated pentachloroaniline; (3) dechlorination to yield tetrachloro analogues of the above metabolites.

Figure 1 shows the metabolic pathways.

Rats. Three male and three female rats were given [^{14}C]quintozene in cotton seed oil as a single dose of 5 mg/kg bw by oral intubation. Whole blood was taken at 0, 0.5, 1, 2, 4, 8, 12, 48, 72, 96, 120 and 144 hours after treatment. The average level of ^{14}C reached a maximum after 12 hours. The half-life was calculated to be 22 hours.

Urine and faeces were collected at 24-hour intervals and analysed for ^{14}C activity. Both urinary and faecal excretion showed a sex difference. The total ^{14}C activity in the urine ranged from 7.8 to 12% of the dose in the males and 24 to 38% in the females. That in the faeces ranged from 57 to 91% in the males and 38 to 76% in the females.

After 144 hours, when the rats were killed, various organs were combusted to determine the ^{14}C activity. The liver, kidneys and carcase contained an average of 0.03, 0.02 and 0.2% of the dose, respectively. The total recovery of ^{14}C from the six animals averaged 85%.

In another study, ten female rats were dosed with 5 mg/kg [^{14}C]quintozene. After 72 hours 32% of the dose was recovered from the urine. The major metabolite was identified as *N*-acetyl-*S*-pentachlorophenylcysteine, which accounted for 59% of the ^{14}C in the urine. A further 24% was identified as a conjugate of pentachloroaniline, 5% as pentachlorophenol and traces as methyl pentachlorophenyl sulfone, methyl pentachlorophenyl sulfide and tetrachlorophenol.

The faeces contained mainly pentachloroaniline (PCA) and phenols, but much of the

radioactivity remained bound (Adamovics, 1980; O'Grodnick, 1978a,b, 1979).

Goats. In a study by Daun (1990) two lactating goats were dosed with [^{14}C]quintozene labelled uniformly in the ring for five consecutive days before slaughter, one at 20 and the other at 50 mg/kg bw/day. Analysis of tissues, milk, urine, and faeces from the high-dose animal indicated that the majority of the activity was eliminated in the urine and faeces (38% and 19% of the dose respectively). The highest concentrations of the remaining activity were found in the kidneys (49 mg/kg as quintozene equivalents) and liver (46 mg/kg). Renal fat contained slightly higher concentrations of ^{14}C than omental fat (33 mg/kg v 27 mg/kg). The lowest concentrations of radioactivity were found in the blood (9.8 mg/kg), milk (5.2 to 8.4 mg/kg) and muscle (2.3 mg/kg). A total of 0.41% of the dose was excreted in the milk over the test period. The low-dose animal showed a similar distribution of radioactivity at lower levels, except in the faeces where 26% of the dose was eliminated.

McManus (1989) identified the metabolites in the high-dose animal. The major metabolite of the four found in the urine accounted for 85% of the urinary radioactivity and was identified as pentachloroaniline sulfamate. The three minor components were *N*-pentachlorophenylhydroxylamine (*N*-hydroxylated pentachloroaniline), tetrachlorothioanisole, and a conjugate of pentachloroaniline (PCA).

The liver, kidneys, fat and muscle (investigated later) showed radioactive levels above background. Six metabolites were identified in the kidneys, of which two accounted for more than 80% of the radioactivity. They were identified as PCA and PCA glucuronide. The four minor metabolites were pentachlorothiophenol, tetrachloro(methylthio)benzenethiol, tetrachlorothioanisole and tetrachloromethylsulfinylaniline (methyl tetrachloroaniline sulfoxide).

Six metabolites were detected in the liver, mainly PCA and a PCA glucuronide conjugate. Trace amounts of four other products were found: pentachlorothiophenol dimer, *N*-pentachlorophenylhydroxylamine, pentachlorothiophenol and tetrachloro(methylthio)benzenethiol.

Milk, omental fat and renal fat each contained only one metabolite which was identified as PCA. No unchanged quintozene was detected in the tissues, milk or urine. The metabolic pathway is mainly reduction to PCA followed by conjugation to form polar products that can be hydrolyzed to PCA. The presence of thiol metabolites indicated that displacement of the nitro group by glutathione also occurred.

The results show that quintozene is converted in goats mainly to PCA and a PCA glucuronide conjugate. Some thiols are also formed to a much smaller extent. The quantitative distribution of the metabolic products in the urine, kidneys, liver, milk and fat is shown in Table 1. These results are in good agreement with those reported previously in a ruminant metabolism study by Aschbacker and Feil (1983) at comparable treatment rates.

Table 1. Distribution of quintozene metabolites in a goat (McManus, 1989).

Sample	Metabolite, % of ^{14}C in sample									
	II	III	IV	V	VI	VII	VIII	IX	X	XI
Urine	85	5	6	4						
Kidneys			4.5		3.3	2.1	26	2.3		55
Liver		4.7	1		2.9		17		2.7	73
Milk							96			
Omental fat							100			

Sample	Metabolite, % of ^{14}C in sample									
	II	III	IV	V	VI	VII	VIII	IX	X	XI
Renal fat							100			

II pentachloroaniline sulfamate
III *N*-pentachlorophenylhydroxylamine (*N*-hydroxypentachloroaniline)
IV tetrachloro(methylthio)benzenethiol
V pentachloroaniline mercapturic acid
VI pentachlorothiophenol
VII tetrachloroanisole
VIII pentachloroaniline
IX tetrachloromethylsulfinylaniline (methyl tetrachloroaniline sulfoxide)
X pentachlorothiophenol dimer
XI *N*-glucuronide of pentachloroaniline

The muscle samples were investigated in an additional study (McManus, 1990a). The total radioactive residue in the muscle was 2.2 mg/kg expressed as quintozene equivalents. Analysis by HPLC showed four metabolites: PCA, tetrachlorothioanisole, pentachlorothiophenol, and methyl tetrachlorophenyl sulfoxide. No unchanged quintozene was detected.

Chickens. Laying hens were treated with [^{14}C]quintozene uniformly labelled in the ring (Parkins 1990a,b, 1991). Three groups of 5 hens were dosed orally by capsule for six consecutive days at 15, 37.5 and 75 mg quintozene per hen per day, with a fourth group as controls. The average feed consumption was approximately 150 g per hen per day, so the doses were equivalent to dietary levels of about 100, 250 and 500 ppm. Table 2 shows the levels of total ^{14}C in the tissues, eggs and excreta.

Table 2. Total ^{14}C residues in tissues and eggs of hens (Parkins, 1990a).

Sample	Residues, mg/kg as quintozene		
	15 mg/day	37.5 mg/day	75 mg/day
Liver	0.87	2.7	3.8
Kidneys	1.8	5.1	7.3
Thigh muscle	0.13	0.36	0.71
Breast muscle	0.07	0.17	0.30
Fat	2.6	6.2	10
Skin (with fat)	1.7	3.8	5.9
Egg yolk	1.7	3.5	5.8[1]
Egg white	0.06	0.24	0.29[1]

[1] Day 5

The major metabolic pathway appears to involve the displacement of the nitro group by the sulfhydryl group of glutathione, followed by catabolic cleavage of the peptide. This pathway led to pentachlorothioanisole, pentachlorothiophenol and conjugates of pentachlorothiophenol with cysteine, malonocysteine, pyruvate and acetate in various tissues, eggs and excreta. Other metabolites included tetrachlorothioanisole, tetrachlorothioanisole sulfone, pentachlorothioanisole sulfoxide and tetrachloromethylsulfinylaniline (methyl tetrachloroaniline sulfoxide). A second pathway involved reduction of the nitro group to produce pentachloroaniline and *N*-pentachlorophenylhydroxylamine

(*N*-hydroxypentachloroaniline).

Table 3 shows the percentage distribution of all metabolites found in the highest dose group (500 ppm) of the study by Parkins (1990a). The levels of ^{14}C in the breast muscle and egg whites were too low for the isolation and identification of metabolites.

quintozene

Figure 1. Metabolism of quintozene in animals.

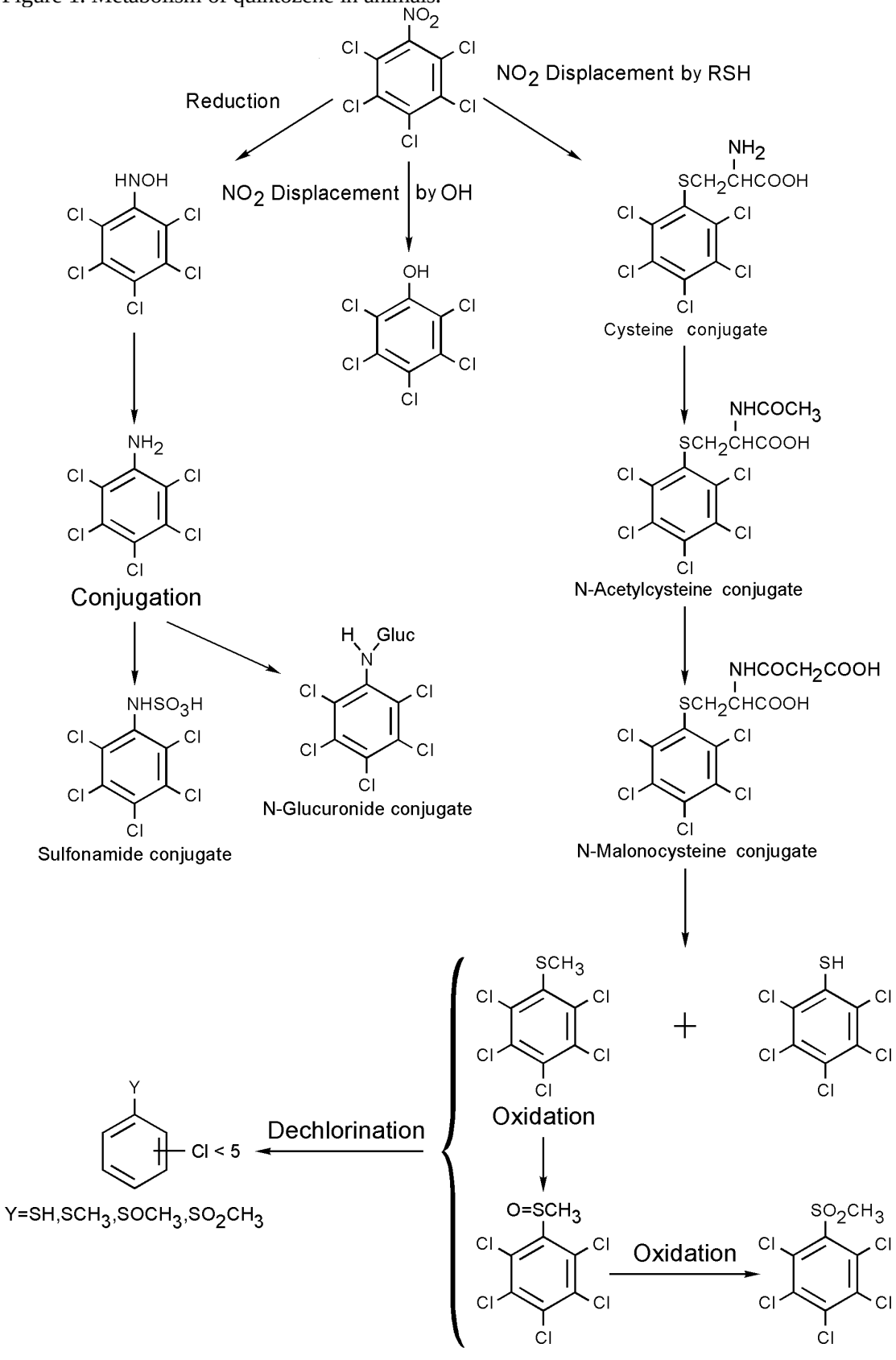


Table 3. Distribution of quintozene metabolites in chickens (Parkins, 1990a).

Sample	Metabolite, % of ^{14}C in sample													
	III	VIII	IX	XII	XIII	XIV	XV	XVI	XVII	XVIII	XVIV	XX	XXI	XXII
Fat		16	31		48								1	
Liver							21	71		7				
Kidneys	50								8	35				7
Thigh						8				88[1]				88[1]
Yolk		70		4		9		18						
Excreta								30		17	26	19		

III *N*-pentachlorophenylhydroxylamine (*N*-hydroxypentachloroaniline)
VIII pentachloroaniline
IX tetrachloromethylsulfinylaniline (methyl tetrachloroaniline sulfoxide)
XII pentachlorobenzene
XIII pentachloronitrobenzene
XIV pentachlorothioanisole
XV pentachlorothioanisole sulfoxide
XVI pentachlorothiophenol
XVII *S*-(pentachlorophenyl)cysteine
XVIII *S*-pentachlorophenyl thioacetate
XVIV *S*-pentachlorophenyl thiopyruvate
XX *S*-(pentachlorophenyl)-*N*-malonyocysteine
XXI tetrachlorothioanisole
XXII tetrachlorothioanisole sulfone

[1] Either XVIII or XXII

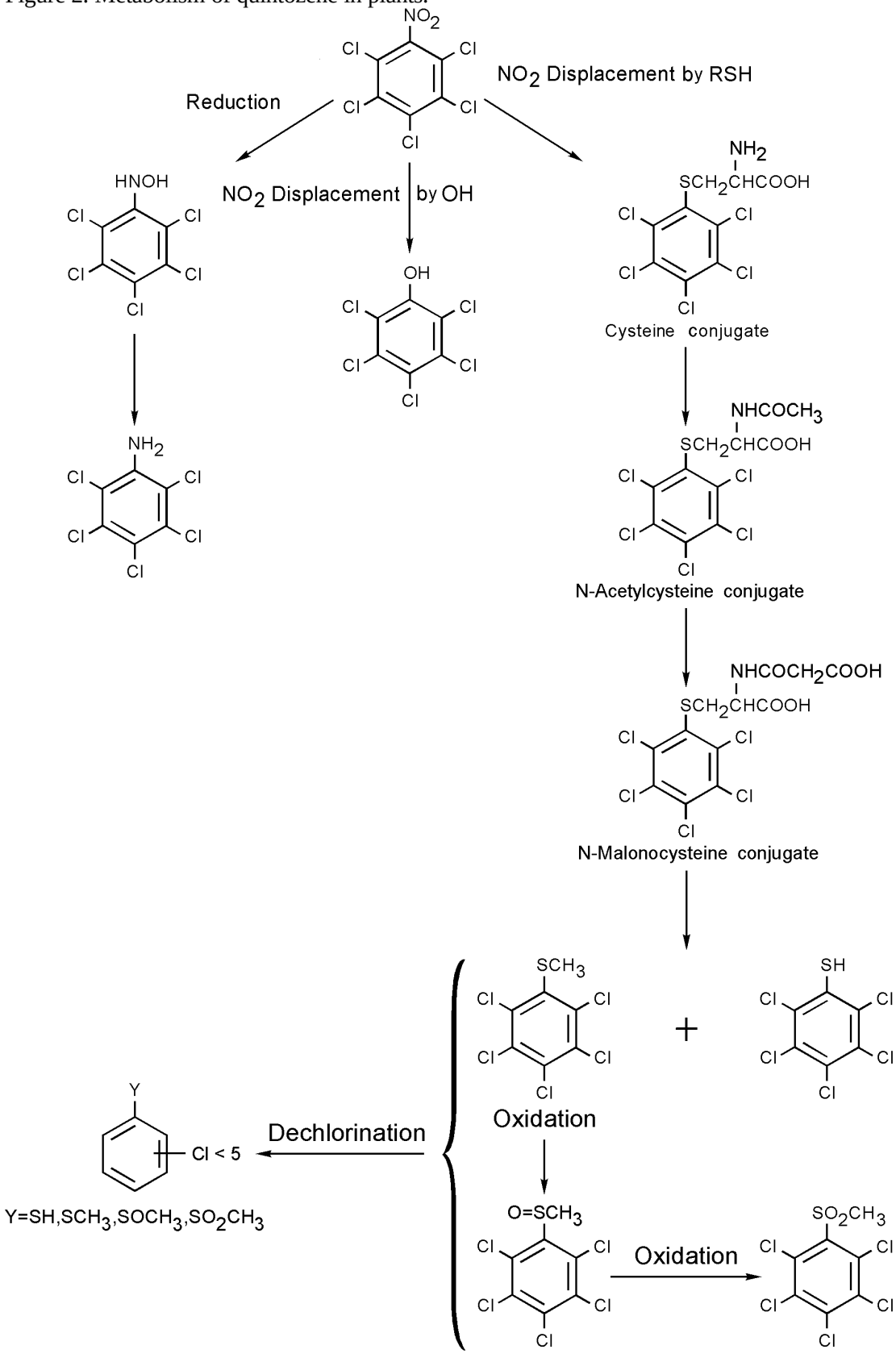
Plant metabolism

Studies of the metabolism of quintozene in cabbages (McManus and Maisonet, 1990), potatoes (Parkins, 1990c) and peanuts (McManus, 1990b) indicated three major pathways, broadly similar to those in animals: (1) reduction of the nitro group to form *N*-pentachlorophenylhydroxylamine (*N*-hydroxypentachloroaniline) and pentachloroaniline; (2) displacement of the nitro group (a) by the sulfhydryl group of glutathione to give a glutathione adduct which is metabolized further, and (b) to a lesser extent by a hydroxyl group to give pentachlorophenol; (3) dechlorination involving (a) reductive replacement of Cl by H and (b) oxidative replacement of Cl by OH.

Figure 2 shows the pathways.

quintozene

Figure 2. Metabolism of quintozene in plants.



The results agree well with those reported in the literature for peanuts (Lamoureaux *et al*., 1980, 1981), onions (Begum *et al*., 1979), spinach (Cairns *et al*., 1983), parsnips (Cairns *et al*., 1987) and cress (Renner and Hopfer, 1983).

Cabbages. Cabbage plants were grown in soil treated with a single application of [^{14}C]quintozene before planting, at 54 kg ai/ha. Plants were harvested at approximately one-quarter, one-half and full maturity (after 49, 70 and 154 days respectively). The two earlier samples of whole plants showed concentrations of radioactivity ranging from 5 to 8 mg/kg as quintozene. The highest levels of radioactivity were found at maturity in the outer leaves (11-18 mg/kg), with lower levels in the heads of 0.79-2.6 mg/kg. Seven metabolites observed in leaf extracts were identified. The two main compounds were methyl tetrachlorophenyl sulfoxide and methyl tetrachlorophenyl sulfone. Five minor components were identified as a methyl trichlorophenyl sulfoxide, a methyl trichlorophenyl sulfone, *N*-hydroxylated pentachloroaniline, methyl pentachlorophenyl sulfoxide and pentachlorothioanisole.

Potatoes. Potatoes were grown in soil treated with [^{14}C]quintozene applied as an EC formulation by pre-plant incorporation at a rate of 21 kg ai/ha, being exposed to quintozene in the soil for 80 days. The total residues, determined by combustion and calculated as the parent compound, were 2.4 mg/kg in the whole potatoes, 0.76 mg/kg in the potato pulp, and 11 mg/kg in the peel. Most of the radioactivity was solubilized by aqueous methanol and then separated into chloroform-soluble, ether soluble and water-soluble fractions. The distribution of ^{14}C in these fractions was 24% in chloroform, 30% in ether and 45% in water from whole potatoes, 28% in chloroform, 22% in ether and 50% in water from pulp, and 71%, 14% and 15% respectively from peel.

The chloroform fraction contained mainly quintozene and pentachloroaniline with lesser amounts of pentachlorothioanisole, tetrachloronitrobenzene, tetrachlorophenol, and *N*-pentachlorophenylhydroxylamine. Ether- and water-soluble residues were mainly conjugates of pentachlorothiophenol, notably with *S*-glycosides, glutamylcysteine, malonocysteine and cysteine.

Peanuts. Peanuts were planted in soil that had been treated with [^{14}C]quintozene at a rate of 38 kg ai/ha and grown to maturity. The highest levels of ^{14}C were found in the roots (1520 mg/kg expressed as quintozene). The vines, shells and kernels had lower residues ranging from 42 mg/kg in the vines to 5.2 mg/kg in the kernels. Extraction with aqueous methanol removed 64-88% of the ^{14}C. The extract contained seven metabolites; the two main ones were identified as *S*-pentachlorophenyl-*N*-malonocysteine and tetrachloroaniline, which were found in the roots, vines and shells. Of the five minor metabolites, one was identified as *S*-[(methylthio)tetrachlorophenyl]-2-thioacetic acid. The other four metabolites were also found in roots, vines, shells and kernels, but at too low a level for identification.

The unextractable ^{14}C residues ranged from 454 mg/kg (as quintozene) in the roots to 0.94 mg/kg in the kernels. An average of more than 90% of these residues in the shells, vines and kernels was liberated by hydrolysis with methanolic HCl.

Seed treatment. Seeds of maize, peas, sugar beet, wheat and soya bean were treated with [^{14}C]quintozene at the highest recommended rates (Selman, 1988). The treated crops were grown in an open-sided greenhouse which allowed exposure to natural sun and weather conditions while eliminating the potential for flooding from rain. There was uptake of [^{14}C] by all the crops. The highest levels were measured in the harvested pea vines and soya bean stems at 1.8 and 1.5 mg/kg quintozene equivalents respectively. The levels in fresh pea vines, sugar beet roots, soya bean hay and wheat forage were 0.57, 0.46, 0.74, and 0.54 mg/kg respectively, and in maize stover and wheat straw 0.02 and 0.06 mg/kg. None of the harvested seeds or grains from maize, wheat, soya bean or peas

contained residues above the LOD.

Rotational crops. Soil was treated with uniformly ring-labelled [^{14}C]quintozene and aged for periods of 30, 120 and 365 days before planting rotational wheat, lettuce and turnips (Murty, 1993). The metabolites were characterized as described above. Considering the high treatment rate of 280 kg ai/ha, the levels of radioactivity found in the lettuce, turnips and wheat grain were not high and they decreased with the age of the soil. The total residues as quintozene equivalents after 365 days were 0.44 mg/kg in lettuce, 1.4 mg/kg in turnip roots and 0.42 mg/kg in wheat grain.

Environmental fate in soil and in water/sediment systems

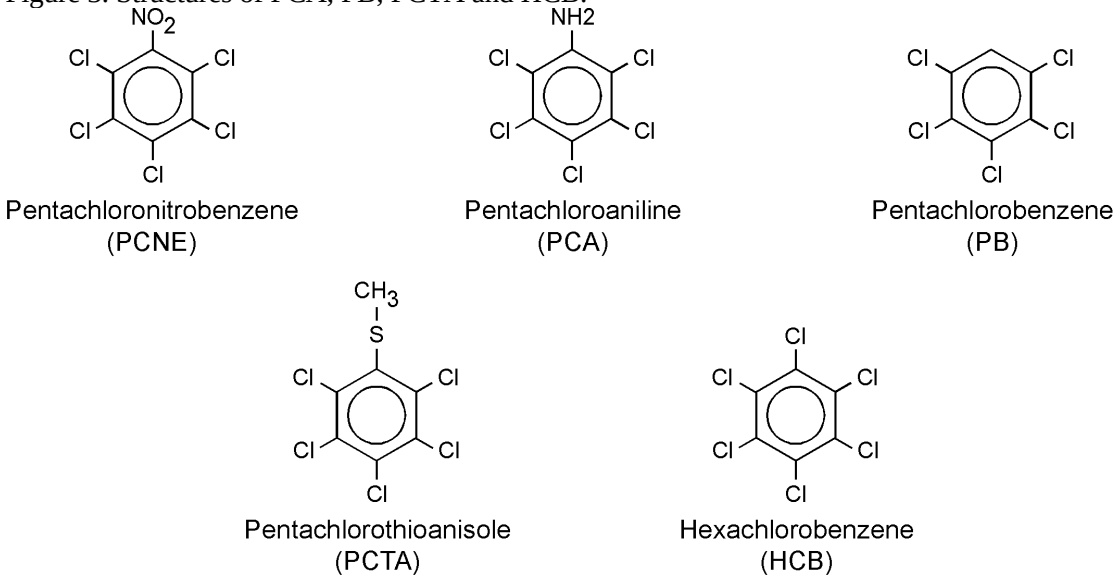
No data were available.

METHODS OF RESIDUE ANALYSIS

Analytical methods

Residues of quintozene, hexachlorobenzene (HCB), pentachlorobenzene (PB), pentachloro-thioanisole (PCTA) and pentachloroaniline (PCA) are determined by GLC with electron-capture detection. The structures of the compounds of interest are shown in Figure 3.

Figure 3. Structures of PCA, PB, PCTA and HCB.



Samples are ground or homogenized in a blender with hexane. The resulting solution is centrifuged, the supernant decanted and filtered, and the residue rinsed with hexane. The combined extracts are evaporated to near dryness and the determination is completed according to the clean-up required.

Oily samples such as peanut kernels and cotton seed are partitioned with acetonitrile and the sample is then extracted several times with a mixture of organic solvents and water. The extracts are combined and dried with anhydrous sodium sulfate, the solvent is evaporated and the residue taken up

in hexane. The hexane solution is filtered and reserved for further GPC and/or Florisil clean-up.

If GPC clean-up is required the sample is eluted with a mixture of toluene and hexane, and the eluate concentrated, evaporated again with petroleum ether, and reserved for clean-up on a Florisil column.

The sample is transferred to a Florisil column topped with a little sodium sulfate and eluted with a small quantity of 3% diethyl ether in petroleum ether. The eluate is concentrated by rotary evaporation under nitrogen and taken up in iso-octane for GLC (Griffith, 1973; Gaydosh, 1990). The limits of detection of quintozene, HCB, PB, PCTA and PCA in vegetables, nuts, oil seeds, milk, eggs and animal tissues ranged from 0.0005 to 0.05 mg/kg, and recoveries from 86 to 104% at fortification levels of 0.025 to 0.2 mg/kg.

In the multi-residue method of The Netherlands (Anon., 1988), the compounds are extracted with a mixture of toluene and 2-propanol. The propanol is removed by washing with water, and the toluene phase is cleaned up with an adsorbent mixture of activated carbon and Celite for the determination of quintozene only or a mixture of Attagel and Hyflo Supercel for the determination of quintozene, PCA and PCTA. After filtration, the compounds are determined by gas chromatography with electron-capture detection (LOD 0.01 mg/kg; recovery >80%).

Stability of pesticide residues in stored analytical samples

Studies of storage stability were conducted on relevant crops (Ball, 1988a, 1990a,b; Gaydosh, 1991a,b) with the results shown in Tables 4-8. It can concluded that residues of quintozene and its metabolites and impurities are stable in head cabbages, kidney beans, potatoes, wheat, cotton seed, and peanuts when stored at -20°C up to one year. A decrease to about 60-70% of the initial level was found in peppers and tomatoes and their processed products after 6 months, and in maize and soya beans after 8 months.

Table 4. Storage stability of quintozene and metabolites added to cotton seed and peanuts at 0.2 mg/kg.

Compound and commodity	Recovery, %, after interval (months)							Ref.
	0	1	2	3	4	6	12	
Cotton seed								
PB	103	98	88	101		92	100	Gaydosh, 1991a
HCB	102	99	86	103		85	101	
quintozene	103	95	86	74		93	99	
PCA	99	98	87	104		88	110	
PCTA	94	98	89	102		102	121	
Peanuts								
PB	98	94	107	98	91	88	106	Gaydosh, 1991b
HCB	97	93	110	102	90	87	109	
quintozene	91	86	111	91	90	90	105	
PCA	96	83	89	93	86	83	112	
PCTA	95	94	105	99	88	89	108	

Table 5. Storage stability of quintozene and metabolites added to tomatoes and their processed products at 0.025 mg/kg (Ball, 1998a).

Compound	Recovery, %, after interval (months)											
	Fruits				Ketchup				Dry pomace			
	0	2	4	6	0	2	4	6	0	2	4	6
PB	88	74	59	60	93	86	52	37	90	71	58	57
HCB	90	79	69	71	94	80	62	54	94	74	60	60
quintozene	89	85	69	72	96	79	61	59	91	73	58	59
PCA	86	82	73	76	91	74	69	60	58	65	56	57
PCTA	90	83	75	78	94	79	69	66	86	71	57	62

Table 6. Storage stability of quintozene and metabolites added to head cabbages and potatoes (Ball, 1990a).

Compound	Spike, mg/kg	Control analytical recovery, %		Recovery after 12 months, %	
		cabbage	potato	cabbage	potato
quintozene	0.2	95	103	91	86
HCB	0.04	98	98	91	85
PCA	0.2	98	90	93	92
PB	0.2	96	101	95	95
PCTA	0.2	99	96	98	96

Table 7. Storage stability of quintozene and metabolites added to peppers and kidney beans at 0.025 mg/kg (Ball, 1988a).

Compound and commodity	Recovery, %, after interval (months)			
	0	2	4	6
Peppers				
PB	94	59	59	48
HCB	96	71	81	58
quintozene	97	67	77	57
PCA	94	70	83	60
PCTA	99	67	85	60
Kidney beans				
PB	102	90	78	82
HCB	104	91	89	90
quintozene	104	91	89	88
PCA	102	97	98	95
PCTA	105	94	98	96

Table 8. Storage stability of quintozene and metabolites added to soya beans (dry), maize and wheat at 0.025 mg/kg (Ball, 1988a).

Compound	Recovery, %, after interval (months)					
	0	2	3	4	6	8
Soya beans (dry)						
PB	100	50	58	81	70	77
HCB	100	54	60	77	67	73
quintozene	98	50	56	75	75	74
PCA	95	58	68	83	83	75
PCTA	98	52	60	75	69	74
Maize						
PB	83	67	77	75	65	65
HCB	91	62	66	80	64	65
quintozene	93	65	92	71	66	69
PCA	95	69	79	80	78	80
PCTA	89	59	69	73	64	69
Wheat						
PB	90	70	86	102	91	125
	93	71	80	98	91	98
quintozene	93	76	62	98	80	88
PCA	95	75	90	98	86	98
PCTA	98	71	84	100	91	91

Residue definition

The Meeting considered that the residue definition for risk assessment purposes for plant and animal commodities should be the sum of quintozene, PCTA and PCA, expressed as quintozene. This definition is also suitable for animal commodities for enforcement purposes since the parent quintozene is not an adequate indicator compound in such commodities. Quintozene alone is a suitable definition of the residue in crops for enforcement purposes. On the basis of the metabolism and animal transfer studies the residue should be described as fat-soluble.

USE PATTERN

Quintozene is applied to garlic, beans, other vegetable seeds, potatoes, cereals and oilseed as a single seed treatment with DS, EC, FS, LS, PS or WP formulations (Table 9), and to bulb, brassica, fruiting, leafy, legume, root and tuber vegetables, pulses, oilseed and coffee beans in one or two soil or plant treatments before or at planting with an EC, DP, GR, SC or WP (Table 10). The PHI is not of importance because the interval between application and harvest is long in most cases. In Spain alone however two or three treatments are registered for peppers and tomatoes, from 15 days post-planting to maturity, but no PHI was reported.

Table 9. Registered uses of quintozene for seed treatment. All single applications.

Crop	Country	Form.	Application

			Rate, kg ai/ha	Concentration, kg ai/hl
Barley	Spain	PS 20%		0.04 -0.2
		PS 24%		0.036-0.19
	USA	FS, DS		0.048-0.11
Beans	Brazil	WP		0.11 -0.23
	USA	FS		0.16 -0.23
Cotton	Australia	WP		0.75 -0.1
		FS		0.1
		LS		0.18 -0.2
	Brazil	WP		0.225-0.45
	Israel	PS	0.75-1.13	0.075-0.11
	South Africa	WP		0.15
	Spain	PS 20%		0.04 -0.2
		PS 24%		0.036-0.19
	Thailand	EC		0.168-1.13
	USA	FS, DS		0.15 -0.2
Garlic	USA	WP 75%		1.0
Oats	USA	FS		0.088-0.18
Maize	Spain	PS 20%		0.04 -0.2
		PS 24%		0.036-0.19
	USA	DS		0.025
		FS		0.048
Peanuts	Brazil	WP		0.22
	Thailand	EC		0.168-1.13
	USA	DS		0.025-0.05
		FS		0.048
Peas	USA	FS		0.048-0.096
Potatoes	Israel	WP		1.0
Safflower	USA	DS		0.025-0.05
Rice	USA	FS		0.064-0.13
Sorghum	USA	DS, FS		0.025
Soya beans	USA	FS		0.048-0.096
Sugar beet	USA	DS		0.075-0.15
		FS		0.088-0.18
Vegetables	New Zealand	WP		0.3[1]
Wheat	Brazil	WP		0.19
	USA	FS		0.048

[1] disinfection of empty seed boxes (0.3 g ai/l/m^2)

Table 10. Registered uses of quintozene for soil and plant treatments.

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
Alfalfa	Saudi Arabia	WP	soil incorp. pre-plant		0.11-0.23		7-10
Beans	Australia	WP	soil incorp. at planting (band)	12-17		1	28
	Cyprus	WP	soil incorp. pre-plant	7.5		1	
	Israel	WP	soil spray in-furrow, pre-plant	0.12		1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	Spain	WP	spray at planting	0.75-2.3		1	
	South Africa	WP	row treatment, pre-plant	3.8		1	
	USA	WP, SC, EC, GR	soil spray in-furrow, at planting	0.84-1.7		1	
Beets	Israel	WP	soil treatment after harvest	600		1	21
Brassica vegetables	Australia	WP	soil drench at planting (band)	12-17		1	28
		WP	seed bed	38-56		1	
	UK	DP	soil incorp. pre-plant	70		1	
	USA	WP, SC, GR	soil treatment, pre-plant (band)		11	1	
	USA	WP, SC, GR	soil incorp. treatment, pre-plant (broadcast)	34	12	1	
	USA	WP, SC	soil drench	8.4-17	2.6-3.9	1	
	USA	WP, SC, EC	soil treatment transplant	0.0005 kg/plant corresp.to ~5 kg ai/ha	0.2	1	
	USA	GR 10%	row applic. to seeding	12-17		1	
Broccoli	Canada	WP	at transplanting		0.18-0.56	1	
	Spain	WP	spray at planting	0.75-2.3		1	
Brussels sprouts	Canada	WP	at transplanting		0.18-0.56	1	
	Spain	WP	spray at planting	0.75-2.3		1	
Cabbages, Head	Canada	WP	at transplanting		0.18-0.56	1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	Spain	WP	spray at planting	0.75-2.3		1	
Cauliflower	Canada	WP	at transplanting		0.18-0.56	1	
	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23	1	
	Spain	WP	spray at planting	0.75-2.3		1	
Coffee	Thailand	EC	soil drench, incorp. pre-plant	108-216	0.18-0.56	1	
Cole Crops	Canada	WP	at transplanting		0.18-0.56	1	
Cotton	Australia	WP	spray at planting	3.8		1	
	Australia	EC	soil treatment in-furrow at planting	1.1-1.7		1	

quintozene

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
	Israel	WP	soil treatment	600 corresp. to 80 g/m^2		1	21
	Saudi Arabia	WP	soil incorp., pre-plant		0.11-0.23		7-10
	Spain	WP	spray at planting	0.75-2.3			1
	South Africa	WP	soil treatment at planting	3.8-5.3			1
	USA	WP, SC, EC, GR	soil spray in-furrow, at planting	0.84-2.3	0.8-1.7	1	
	USA	GR	drill at planting	0.87-1.1		1	
	USA	GR	hill-drop at planting	0.29-0.36		1	
Cucumbers	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	UK	DP	soil incorp. pre-plant	70		1	
Egg plants	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
Endive	UK	DP	dusting, pre-plant	70		1	
Garlic	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	USA	WP, SC, EC, GR	soil spray in-furrow, at planting	22-23		1	
Ginseng	Canada	WP	spray prior to bud break	6.8	0.15-0.2	1	
Leafy herbs	UK	DP	dusting, pre-plant	70		1	
Lettuce	Australia	WP	soil applic. at singling (band)		0.075-0.11	1	28
	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	UK	DP	soil incorp. pre-plant	70		1	
Mushrooms	Cyprus	WP	at planting		0.75	1	
Onions	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
	South Africa	WP	dry dressing seedling, pre-plant or at planting		1.5	1	
	South Africa	WP	soil treatment, pre-plant or at planting	25		1	
Peas	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
Peanuts	Australia	WP	directed spray at pegging	12-17		1-2	28
	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
	Israel	WP	soil treatment, after harvest	600		1	21
	Saudi Arabia	WP	soil incorp., pre-plant		0.11-0.23		7-10
	USA	WP, SC, EC	soil spray in-furrow, at planting	1.1-2.2		1-2	45
	USA	WP, SC, GR	soil applic. at pegging (band)	11		1-2	45
	USA	WP, SC	at cultivation	3.6		1-2	45
	USA	GR	soil-mix cultivation	3.7		1-2	45
	USA	GR	soil applic. split pegging; soil-mix; band	2.8-5.6		1-2	45
Peppers	Cyprus	WP	soil incorp., pre-plant	7.5	75	1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	Spain	EC	irrigation, 15 days post-planting	3.6-6		2-3	

Crop	Country	Form.	Application				PHI, days
			Method	Rate, kg ai/ha	Spray conc., kg ai/hl	No.	
			to maturity[1]				
	Spain	WP	spray at planting	0.75-2.3		1	
	UK	DP	dusting, pre-plant	70		1	
	USA	WP	soil applic. at transpl.	2.5	0.27	1	
	USA	WP	soil spray in-furrow, at planting	5.5-8.4	0.58-0.9	1	
Potatoes	Australia	WP	soil applic. at planting (band)	25-30		1	28
	Cyprus	WP	soil incorp. pre-plant	7.5	75	1	
	Israel	WP	soil incorp.	75		1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	South Africa	WP	soil applic. pre-plant or at planting	23-30		1	
Tomatoes	Australia	WP	soil applic. at transplanting		0.23-0.38	1	28
	Cyprus	WP	spray at planting		0.19	1	
	Saudi Arabia	WP	root drench, post-plant		0.11-0.23		
	Spain	EC	irrigation, 15 days post planting to maturity[1]	3.6-6		2-3	
	Spain	WP	spray at planting	0.75-2.3		1	
	UK	DP	soil incorp. pre-plant	70		1	
	USA	WP 75%	transplant treatment	2.5	0.27	1	
	USA	WP 75%	soil spray in-furrow at planting	5.5-8.4	0.58-0.9	1	
Vegetables	New Zealand	WP	soil applic. pre-plant	90		1	
	New Zealand	WP	drench, post-planting		0.05	1	

[1] field and glasshouse use

RESIDUES RESULTING FROM SUPERVISED TRIALS

The Meeting reviewed US data on supervised residue trials with soil or plant treatment for broccoli, head cabbages, peppers, tomatoes, beans, potatoes, cotton seed and peanuts, and with seed treatment for sugar beets, peas, barley, maize and soya beans. Residues of quintozene (PCNB), its metabolites pentachlorothioanisole (PCTA) and pentachloroaniline (PCA), and the impurities hexachlorobenzene (HCB) and pentachlorobenzene (PB) were determined in all the trials. In the trials before 1990 the technical quintozene contained not more than 0.5% of the impurity HCB. Subsequently the maximum HCB content was reduced to <0.1% by the manufacturer.

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beans (dry).
17 Residues of quintozene, its metabolites and impurities in potatoes.
18 Residues of quintozene, its metabolites and impurities in cotton seed.
19 Residues of quintozene, its metabolites and impurities in peanut.
20 Residues of quintozene, its metabolites and impurities in barley, maize, peas, soya beans and sugar beets after seed treatment.

Residues in crops from soil treatment

Broccoli. Broccoli in Oregon and California were treated by broadcast, band and transplant water applications (Ball, 1988b), and in Oregon also by direct seeded (broadcast) applications. The broccoli were harvested at maturity, a PHI of 64-83 days. Forty eight samples were analysed (Table 11). The residues from direct seeded applications of both WP and GR formulations were lower than those from the other modes of application. Broadcast and band applications gave comparable residues. Plants treated at transplanting had the highest residues.

Table 11. Residues of quintozene, its metabolites and impurities in broccoli, USA, 1993. All single applications.

Application		PHI, days	Residues, mg/kg				
Form, method	kg, ai/ha		PCNB	PB	HCB	PCTA	PCA
WP direct seed	34	73-78	0.004 0.005 0.006 (2)	<0.002 (4)	<0.002 (4)	<0.002 (4)	0.003 (4)
WP broad-cast	34	64-77	<0.002 <0.002 <0.002 0.002 0.003 0.005 0.018 0.023	<0.002 (8)	<0.002 (8)	<0.002 (7) 0.002	<0.002 <0.002 0.002 0.002 0.003 0.004 0.01 0.017
WP band	25	72 - 83	0.004 0.004 0.004 0.006 0.006 0.01 0.02 0.024	<0.002 (8)	<0.002 (8)	<0.002 (7) 0.003	0.003 0.004 0.004 0.005 0.006 0.009 0.012 0.014
WP transplant	5.0	72 - 83	0.017 0.019 0.024 0.027 0.038 0.05	<0.002 (6)	<0.002 (6)	0.005 0.007 0.003 0.002 0.004 0.004	0.016 0.028 0.03 0.015 0.03 0.04
WP drench	5.0	64	0.014 0.015	<0.002 (2)	<0.002 (2)	<0.002 0.003	0.01 (2)
GR direct seed	34	73 - 78	0.004 0.005 0.006 0.009	<0.002 (4)	<0.002 (4)	<0.002 <0.002 <0.002 0.003	0.002 0.002 0.002 0.007
GR band	22	64 -83	0.003 0.007 0.007	<0.002 (8)	<0.002 (8)	0.002 0.002 <0.002	0.004 0.006 0.004

Application		PHI, days	Residues, mg/kg				
Form, method	kg, ai/ha		PCNB	PB	HCB	PCTA	PCA
			0.008 0.009 0.023 0.007 0.023			0.003 <0.002 <0.002 0.003 0.002	0.006 0.003 0.012 0.007 0.016
GR broad-cast	34	73 - 83	0.004 0.006 0.006 0.007 0.008 0.008 0.028 0.027	<0.002 (8)	<0.002 (8)	0.003 <0.002 <0.002 0.002 0.002 0.004 0.002 <0.002	0.004 0.006 0.006 0.006 0.006 0.005 0.021 0.014

Head cabbages. Residue trials on head cabbages (4 varieties of white and 1 of savoy cabbage) were carried out at eight locations in California, Illinois, Florida, New York and Wisconsin, representing the commercial production areas in the USA (Ball, 1988c). The soil was treated with quintozene by broadcast or band application. In the transplant solution treatments the soil was treated after the seedlings were planted. Cabbage plants were grown to maturity (67-125 days after application). Cabbage heads with and without wrapper leaves were analysed (Table 12).

Table 12. Residues of quintozene, its metabolites and impurities in head cabbages, USA, 1987. All single applications (Ball, 1988c).

Application		PHI, days	Residues, mg/kg				
Form, method	kg, ai/ha		PCNB	PB	HCB	PCTA	PCA
With wrapper leaves							
WP broadcast	34	67-125	0.036 0.038 0.041 0.019 0.013 0.009 0.005 <0.002 (4) 0.004 0.006 0.004	<0.002 (12) 0.002 (2)	<0.002 (14)	<0.002 (14)	0.014 0.029 0.025 0.02 0.008 0.005 0.003 <0.002 (4) <0.002 0.005 0.004
WP band	25	67-125	0.005 0.005 0.015 0.015 <0.002 (7) 0.004 0.002 0.002	<0.002 (13) 0.002	<0.002 (14)	<0.002 (14)	0.005 0.005 0.02 0.02 <0.002 (7) 0.003 0.003 0.002
WP transplant solution	5.0	67-125	<0.002 (8) 0.009 0.037 0.062 0.002 0.004 0.005	<0.002 (12) 0.002 0.003	<0.002 (14)	<0.002 (12) 0.006 0.004	<0.002 (8) 0.01 0.038 0.041 0.003 0.003 0.005
GR broadcast	34	67-125	0.01 0.016 0.046 0.014 0.009 0.009 0.003 0.003 <0.002 <0.002 (5)	<0.002 (14)	<0.002 (14)	<0.002 (14)	0.005 0.012 0.03 0.009 0.009 0.003 0.003 0.007 0.002 <0.002 (5)
GR band	22	67-125	0.009 0.009 0.05 0.026 <0.002 (10)	<0.002 (13) 0.003	<0.002 (14)	<0.002 (14)	0.008 0.01 0.042 0.031 <0.002 (10)
Without wrapper leaves							
WP broadcast	34	67-125	0.004 0.003 0.003 <0.002 (10)	<0.002 (13)	<0.002 (13)	<0.002 (13)	0.003 0.003 0.002 <0.002 (10)
WP band	25	67-125	<0.002 (10) 0.002 0.005	<0.002 (12)	<0.002 (12)	<0.002 (12)	<0.002 (10) 0.003 0.003
WP solution	5.0	67-125	<0.002 (9) 0.008 0.004	<0.002 (13)	<0.002 (13)	<0.002 (13)	<0.002 (9) <0.002 0.003

quintozene

Application		PHI, days	Residues, mg/kg				
Form, method	kg, ai/ha		PCNB	PB	HCB	PCTA	PCA
			0.006 0.002				0.004 0.002
GR broadcast	34	67-125	0.016 0.003 0.013 0.01 <0.002 (6) <0.002 <0.002 <0.002	<0.002 (13)	<0.002 (13)	<0.002 (13)	<0.002 (10) 0.003 0.008 0.009
GR band	22	67-125	<0.002 (10) 0.015 0.002 0.012	<0.002 (13)	<0.002 (13)	<0.002 (13)	<0.002 (11) 0.002 0.012

Peppers, sweet. Trials were carried out at six sites in Florida (2), New Jersey (1), Texas (1) and California (2), representing a substantial pepper-growing segment of the USA (Ball, 1988d, 1989a). Applications were by in-furrow treatment and drench at transplanting. Twenty samples of peppers were analysed (Table 13).

Table 13. Residues of quintozene, its metabolites and impurities in peppers, USA, 1957. All single applications of WP formulation.

Application kg, ai/ha	PHI, days	Residues, mg/kg					Reference
		PCNB	PB	HCB	PCTA	PCA	
8.4	104	<0.05 (2)	<0.05 (2)	<0.05 (2)	<0.05 (2)	<0.05 (2)	Ball, 1989a
4.2	104	<0.05 (2)	<0.05 (2)	<0.05 (2)	<0.05 (2)	<0.05 (2)	Ball, 1988d
8.4	71-91	<0.05 (8)	<0.05 (8)	<0.05 (8)	<0.05 (8)	<0.05 (8)	
4.2	71-91	<0.05 (8)	<0.05 (8)	<0.05 (8)	<0.05 (8)	<0.05 (8)	

Tomatoes. Ball (1990c) ran trials at eight locations in California, Florida, Indiana, Michigan and New Jersey, using in-furrow treatments and drench at transplanting. The analytical method used to determine the residues of quintozene, PB, HCB, PCA and PCTA was validated at an LOD of 0.05 mg/kg, at which level no residues were detectable. Eighteen of the original 37 samples were re-analysed (Ball, 1990d) by a modified method with an LOD of 0.002 mg/kg. The results by the modified method are shown in Table 14.

Table 14. Residues of quintozene, its metabolites and impurities in tomatoes, USA 1990. All single applications.

Application		PHI, days	Residues, mg/kg					Reference
Form, method	kg, ai/ha		PCNB	PB	HCB	PCTA	PCA	
WP in-furrow	8.4	73-113	<0.002 (7) 0.003 0.006 0.012	<0.002 (10)	<0.002 (10)	<0.002 (10)	<0.002 (10)	Ball, 1990d
WP transplant solution	3.9	73-113	<0.002 (6) 0.003 (2)	<0.002 (8)	<0.002 (8)	<0.002 (8)	<0.002 (8)	

Common beans (pods and/or immature seeds). Three formulations of quintozene were applied to snap beans at each location in New York, Oregon and North Carolina as a directed spray in the seed furrow (single applications). At all sites the sample consisted of mature snap beans (Gaydosh, 1993). In 1987 quintozene was applied four times to snap and succulent lima beans (Ball, 1988e, 1990e) and the beans harvested at maturity, with a 14-day PHI for snap beans and a 35-day PHI for lima beans. In total, 44 samples were analysed (Table 15).

Table 15. Residues of quintozene, its metabolites and impurities in common beans (pods and/or immature seeds), USA.

Year, commodity	Application			PHI, days	Residues, mg/kg					Ref.
	Form	No.	kg ai/ha		PCNB	PB	HCB	PCTA	PCA	
1993, snap beans	WP	1	1.7	42 -	<0.0005 (2)	<0.0005 (6)	<0.0005	<0.0005	<0.0005 (4)	Gaydosh,

Year, commodity	Application			PHI, days	Residues, mg/kg					Ref.
	Form	No.	kg ai/ha		PCNB	PB	HCB	PCTA	PCA	
				62	0.012 0.014 0.043 0.053		(6)	(6)	 0.007 0.007	1993
	EC	1	1.7	42 - 62	<0.0005 (2) 0.081 0.068 0.017 0.018	<0.0005 (6)	<0.0005 (6)	<0.0005 (4) 0.01 0.007	<0.0005 (2) 0.01 0.009 0.008 0.007	
	SC	1	1.7	42 - 62	<0.0005 (2) 0.069 0.062 0.012 0.013	<0.0005 (6)	<0.0005 (6)	<0.0005 (4) 0.006 0.007	<0.0005 (3) 0.006 0.007 0.006	
1987, lima beans	EC	4	2.2	35	0.009 0.012 0.026 <0.002 0.003 0.006	<0.002 (6)	<0.002 (6)	<0.002 <0.002 0.002 <0.002 <0.002 <0.002	0.007 0.004 0.01 <0.002 <0.002 <0.002	Ball, 1988e, 1990e
	WP	4	2.2	35	0.004 0.009 0.025 0.003 0.004 0.006	<0.002 (6)	<0.002 (6)	<0.002 <0.002 0.003 <0.002 (3)	<0.002 0.003 0.01 0.003 0.002 <0.002	
1987, snap beans	EC	4	2.2	14	0.021 0.033 0.031 0.01 0.047 0.029	<0.002 (6)	<0.002 (6)	<0.002 0.004 0.005 <0.002 0.008 <0.002	0.004 0.007 0.019 0.041 0.043 0.047	
	WP	4	2.2	14	0.016 0.021 0.037 0.01 0.13 0.041 0.007 0.06	<0.002 (8)	<0.002 (8)	<0.002 0.002 0.005 <0.002 (5)	0.004 0.005 0.006 0.024 0.025 0.026 0.053 0.1	

Common beans (dry). In trials in 1993 in Michigan, North Dakota, and California three common varieties of beans were treated by single ground applications and samples of mature beans were analysed (Gaydosh, 1994a). In 1987 kidney, navy and pinto beans were treated with four applications of quintozene. The first spray treatment was pre-emergence, the second and the third at plant heights of 7.5 and 20 cm, and the fourth at row closure (Ball, 1988e, 1990e). Beans were harvested at maturity, 35-78 days after treatment. In total 37 samples were analysed (Table 16).

Table 16. Residues of quintozene, its metabolites and impurities in common beans (dry), USA.

Year, commodity	Application	PHI, days	Residues, mg/kg	Ref.

	Form	No	kg ai/ha		PCNB	PB	HCB	PCTA	PCA	
1993, dry red kidney beans, pinto beans	WP	1	1.7	77 - 106	<0.0005 (4) 0.005 0.004	<0.0005 (6)	<0.0005 (6)	<0.0005 (6)	<0.0005 (4) 0.002 0.001	Gaydosh, 1994a
	EC	1	1.7	77 - 106	<0.0005 (4) 0.013 0.02	<0.0005 (5) 0.001	<0.0005 (6)	<0.0005 (5) 0.002	<0.0005 (4) 0.003 0.007	
	SC	1	1.7	77 - 106	<0.0005 (4) 0.008 0.005	<0.0005 (6)	<0.0005 (6)	<0.0005 (5) 0.0006	<0.0005 (4) 0.0015 (2)	
1987, dry red kidney beans; navy beans; pinto beans	WP	4	2.2	35 - 78	<0.002 (5) 0.029 0.013 0.015 0.017 0.003	<0.002 (10)	<0.002 (10)	<0.002 (10)	<0.002 (5) 0.01 0.009 0.006 0.004 <0.002	Ball 1988e, 1990e
	EC	4	2.2	35 - 78	<0.002 (4) 0.021 0.01 0.028 0.052 0.009	<0.002 (9)	<0.002 (9)	<0.002 (9)	<0.002 (4) 0.019 0.009 0.005 0.009 <0.002	

Potatoes. In residue trials by Ball (1988f) at 12 locations in 10 States (Florida, Oregon, Michigan, Maine, Minnesota, Washington, California, Idaho, North Dakota and Wisconsin) potatoes were treated in-furrow and by broadcast applications and harvested at maturity, after 3-4.5 months. The analytical method used to determine the residues of quintozene, PB, HCB, PCA and PCTA was validated at an LOD of 0.002 mg/kg. The results (Table 17) showed higher residues of quintozene from the in-furrow applications. Of the five compounds determined, quintozene, PCA and PCTA were present at the highest levels.

Table 17. Residues of quintozene, its metabolites and impurities in potatoes, USA, 1987. Single applications (Ball, 1988f).

Form	kg, ai/ha	PHI, days	PCNB, mg/kg	PB, mg/kg	HCB, mg/kg	PCTA, mg/kg	PCA, mg/kg
EC broad-cast	28	82-136	0.15 0.16 0.05 0.05 0.082 0.11 0.052 0.052 0.082 0.005 0.01 0.07 0.008 0.14 0.14 0.14 <0.002 (5) 0.017 0.014 0.023 0.013 0.016	0.058 0.052 0.028 0.022 0.029 0.038 0.019 0.031 0.003 0.004 0.020 0.006 0.014 0.014 0.11 0.089 <0.002 (5) 0.068 0.056 0.023 0.014 0.03	0.007 0.008 0.005 0.003 0.01 0.01 0.007 0.01 <0.002 <0.002 0.005 0.005 0.003 0.024 0.02 0.018 <0.002 (5) 0.004 0.004 0.003 <0.002 0.004	0.05 0.05 0.026 0.019 0.054 0.062 0.031 0.057 <0.002 <0.002 0.044 0.033 0.01 0.3 0.16 0.13 <0.002 (5) 0.01 0.006 0.01 0.004 0.015	0.11 0.087 0.020 0.015 0.03 0.03 0.024 0.025 0.045 0.002 0.003 0.023 0.029 0.01 0.2 0.16 <0.002 (5) 0.056 0.046 0.026 0.012 0.03

Form	kg, ai/ha	PHI, days	PCNB, mg/kg	PB, mg/kg	HCB, mg/kg	PCTA, mg/kg	PCA, mg/kg
			0.012 0.004 0.009	0.015 0.005 0.012	0.002 <0.002 <0.002	0.007 0.004 0.01	0.01 0.004 0.009
EC in furrow	11	82-135	0.033 0.021 0.33 0.17 0.2 0.12 0.08 0.96 0.81 0.03 0.024 0.026 0.21 0.15	0.03 0.027 0.036 0.022 0.019 0.034 0.022 0.064 0.041 0.008 0.017 0.011 0.045 0.052	0.003 0.002 0.019 0.013 0.013 0.007 0.005 0.033 0.022 0.003 0.003 0.003 0.014 0.014	0.017 0.01 0.10 0.042 0.059 0.033 0.021 0.24 0.17 0.014 0.013 0.012 0.19 0.17	0.044 0.033 0.058 0.036 0.044 0.04 0.024 0.25 0.2 0.01 0.021 0.017 0.13 0.13
EC in furrow	13	103-135	0.34 <0.002 0.29 0.072 0.076 0.21 0.39 0.26	0.022 <0.002 0.03 0.028 0.011 0.023 0.011 0.007	0.011 <0.002 0.007 0.003 0.002 0.006 0.009 0.006	0.052 <0.002 0.034 0.01 0.01 0.035 0.06 0.046	0.049 <0.002 0.01 0.053 0.028 0.014 0.013 0.041

Cotton seed. Seven trials in 1988 (Gaydosh, 1992) in California (2), Louisiana (2), Mississippi (2) and Georgia (1) were with single in-furrow treatments. The crops were sampled at maturity, about four to five months after the application. The analytical method used to determine the residues of quintozene PB, HCB, PCA and PCTA was validated at a LOD of 0.005 mg/kg.

In 1994 Gaydosh (1994b) carried out trials in two growing regions, in Mississippi and Texas, with single ground applications in-furrow at planting. Mature cotton was harvested at both sites (Mississippi 142-day PHI, Texas 160-day PHI) and ginned to provide cotton seed. The analytical method used at an LOD of 0.002 mg/kg for all the analytes. The results are shown in Table 18.

Peanuts. In trials in 1988 (Ball, 1989b) at three locations in Virginia (1) and Georgia (2), peanut plants were treated by small-scale irrigation at pegging and 45 days before harvest. The analytical method had an LOD of 0.005 mg/kg for all the compounds determined.

In three trials by Gaydosh (1994c,d,e) in Georgia, Oklahoma and Texas, applications were also at pegging and again 45 days before harvest. The analytical method used in the first trial (1994c) had an LOD of 0.005 mg/kg for quintozene, PB, PCA and PCTA and 0.001 mg/kg for HCB, and that in the other trials (1994d,e) had LODs of 0.001 mg/kg and 0.0005 mg/kg respectively. In all three trials mature peanuts were harvested and the kernels and hulls analysed (Table 19).

Table 18. Residues of quintozene, its metabolites and impurities in cotton seed, USA. All single applications at 2.2 kg ai/ha.

Year	Form	PHI, days	Residues, mg/kg					Ref.
			PCNB	PB	HCB	PCTA	PCA	

Year	Form	PHI, days	Residues, mg/kg					Ref.
			PCNB	PB	HCB	PCTA	PCA	
1988 1988	EC	140-166	<0.005 (13) 0.008	<0.005 (14)	<0.005 (14)	<0.005 (14)	<0.005 (12) 0.008 0.014	Gaydosh, 1992
	FL	140-166	<0.005 (14)	<0.005 (14)	<0.005 (14)	<0.005 (13) 0.010	<0.005 (12) 0.008 0.009	
1994	G	142-160	<0.002 (4)	<0.002 (4)	<0.002 (4)	<0.002 (4)	<0.002 (3) 0.002	Gaydosh, 1994b
	EC	142-160	<0.002 (4)	<0.002 (4)	<0.002 (4)	<0.002 (4)	<0.002 0.002 (3)	

Table 19. Residues of quintozene, its metabolites and impurities in peanuts, USA. Two applications.

Year, sample	Application		PHI, days	Residues, mg/kg					Ref.
	Form	kg ai/ha		PCNB	PB	HCB	PCTA	PCA	
1988, kernel	EC	2 x 5.6	45	0.008 0.006 0.17 0.23 0.25 0.17	<0.005 <0.005 0.034 0.047 0.045 0.027	<0.005 <0.005 <0.005 <0.005 0.006 0.005	<0.005 <0.005 0.028 0.039 0.04 0.036	<0.005 <0.005 0.052 0.072 0.07 0.056	Ball, 1989b Project No. RP-88002
hull				<0.005 0.007 0.45 0.70 0.37 0.43	<0.005 <0.005 0.050 0.074 0.043 0.043	<0.005 <0.005 <0.005 <0.005 0.005 0.005	<0.005 <0.005 0.10 0.16 0.075 0.096	<0.005 <0.005 0.13 0.21 0.10 0.14	
1988, kernel	SC	2 x 4.7	45	<0.005 (2)	<0.005 (2)	<0.005 (2)	<0.005 (2)	<0.005 (2)	Ball, 1989b Project No. RP-88002
hull				<0.005 0.056	<0.005 <0.005	<0.005 <0.005	<0.005 <0.005	<0.005 <0.005	
1994, kernel	WP	6.7 4.5	45	0.007 0.008 0.006 0.005	0.011 0.008 0.006 0.008	0.002 0.001 0.001 0.001	0.004 0.004 0.003 0.003	0.015 0.016 0.02 0.019	Gaydosh, 1994c
hull				0.014 0.033 0.018 0.018	0.001 0.004 0.004 0.009	<0.001 0.001 0.003 0.018	0.005 0.012 0.012 0.003	0.015 0.044 0.023 0.038	
1994, kernel	GR	2 x 5.6	45	0.051 0.048 0.045 0.007	0.012 0.012 0.009 0.005	0.0035 0.0048 0.0094 0.0016	0.017 0.016 0.01 0.002	0.025 0.02 0.045 0.014	Gaydosh, 1994d
hull				0.85 0.94 0.056 0.092	0.027 0.032 0.003 0.003	0.012 0.013 0.0005 0.0006	0.21 0.19 0.006 0.008	0.2 0.16 0.023 0.032	
1994, kernel	WP	7.8 3.6	45	0.005 0.005 0.002 0.002	0.008 0.008 0.002 <0.001	0.0059 0.0028 0.0024 <0.0005	0.004 0.005 0.002 <0.001	0.011 0.011 0.01 0.008	
hull				0.034	0.006	0.0014	0.035	0.025	

Year, sample	Application		PHI, days	Residues, mg/kg					Ref.
	Form	kg ai/ha		PCNB	PB	HCB	PCTA	PCA	
				0.047 0.006 0.006	0.003 <0.001 0.001	0.0013 0.0007 0.0007	0.039 <0.001 <0.001	0.029 0.018 0.017	
1994, kernel	EC	2 x 2.6	45-47	0.13 0.11 0.045 0.037 0.15 0.15	0.06 0.066 0.020 0.022 0.056 0.046	0.008 0.0064 0.0025 0.0022 0.016 0.017	0.065 0.06 0.006 0.005 0.11 0.12	0.17 0.14 0.05 0.05 0.16 0.16	Gaydosh, 1994e
hull				0.13 0.10 0.31 0.37 0.28 0.29	0.034 0.032 0.022 0.016 0.12 0.18	0.0033 0.0025 0.0019 0.0023 0.0029 0.0024	0.065 0.057 0.034 0.033 0.16 0.17	0.13 0.11 0.25 0.3 0.27 0.27	
kernel	SC	2 x 4.7	45-47	0.047 0.04 0.01 0.011 0.058 0.068	0.014 0.014 0.003 0.004 0.027 0.060	0.0022 0.0027 0.001 0.001 0.01 0.007	0.011 0.01 <0.001 0.001 0.046 0.052	0.043 0.037 0.011 0.015 0.077 0.086	
hull				0.055 0.051 0.069 0.071 0.11 0.085	0.014 0.009 0.003 0.003 0.092 0.065	0.002 0.001 0.0011 0.0015 0.0028 0.0014	0.022 0.021 0.005 0.007 0.082 0.083	0.048 0.043 0.041 0.045 0.13 0.12	

Residues in crops from seed treatment

Sixty two US residue trials with quintozene applied as a seed treatment were carried out on peas(dry) in Idaho, New York, California and Montana, on sugar beet in Idaho, North Dakota, California and Montana, on barley in Idaho, North Dakota, Oregon, California and Montana, on maize in Illinois, Oklahoma, Ohio, New York, Missouri and Virginia, on wheat in North Dakota (2), Idaho, Mississippi, California, Ohio, Oregon and Kansas, and on soya beans in Montana, Illinois, Ohio, Iowa, Missouri, Mississippi, Virginia and Georgia (Gaydosh, 1991c-h). The results are shown in Table 20.

Table 20. Residues of quintozene, its metabolites and impurities in barley, maize, wheat, peas, soya beans and sugar beets after seed treatment, USA, 1987. All single applications of FS.

Crop	kg ai/100 kg seed	Sample	Residues, mg/kg					Ref.
			PCNB	PB	HCB	PCTA	PCA	
barley	0.13	forage, green[1]	<0.005 (5) 0.11	<0.005 (6)	<0.005 (6)	<0.005 (5) 0.009	<0.005 (5) 0.013	Gaydosh, 1991c
		grain	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	
		straw	<0.005 (4)	<0.005 (4)	<0.005 (4)	<0.005 (4)	<0.005 (4)	
maize	0.052	whole plant	<0.005 (14)	<0.005 (14)	<0.005 (13) 0.019	<0.005 (14)	<0.005 (14)	Gaydosh, 1991d
		ear with husk, milk-stage	<0.005 (14)	<0.005 (14)	<0.005 (13) 0.01	<0.005 (14)	<0.005 (14)	
		forage, milk-stage	<0.005 (13)	<0.005 (13)	<0.005 (13)	<0.005 (13)	<0.005 (13)	

Crop	kg ai/100 kg seed	Sample	Residues, mg/kg					Ref.
			PCNB	PB	HCB	PCTA	PCA	
		grain, mature	<0.005 (12)	<0.005 (12)	<0.005 (12)	<0.005 (12)	<0.005 (12)	
		fodder, mature	<0.005 (12) 0.006	<0.005 (13)	<0.005 (13)	<0.005 (13)	<0.005 (13)	
wheat	0.052	forage, green[1]	<0.005 (6) 0.028 0.04 0.011 0.019 0.38 0.82	<0.005 (10) 0.009 0.008	<0.005 (10) 0.006 0.008	<0.005 (10) 0.018 0.014	<0.005 (8) 0.009 0.008 0.006 0.007	Gaydosh, 1991h
		grain	<0.005 (19) 0.0061	<0.005 (20)	<0.005 (20)	<0.005 (20)	<0.005 (20)	
		straw	<0.005 (17) 0.006 0.007 0.023	<0.005 (20)	<0.005 (19) 0.014	<0.005 (20)	<0.005 (20)	
peas	0.12	peas with pods	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	Gaydosh, 1991e
		pea forage	<0.005 (4) 0.006 (2) 0.01 0.011	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	
		peas, dried	<0.005 (6) 0.005 0.007	<0.005 (8)	<0.005 (8)	<0.005 (8)	<0.005 (8)	
		hay, dried	0.013 0.02 0.016 0.015 <0.005 <0.005 <0.005 <0.005	<0.005 (8)	<0.005 (8)	<0.005 <0.005 0.009 <0.005 <0.005 <0.005 <0.005 <0.005	0.008 0.015 <0.005 <0.005 0.006 <0.005 <0.005 <0.005	
soya beans	0.10	whole plant, green[1]	<0.005 (16)	<0.005 (16)	<0.005 (16)	<0.005 (16)	<0.005 (16)	Gaydosh, 1991f
		whole plant at harvest	<0.005 (14)	<0.005 (14)	<0.005 (14)	<0.005 (14)	<0.005 (13) 0.014	
		beans at harvest	<0.005 (16)	<0.005 (16)	<0.005 (16)	<0.005 (16)	<0.005 (16)	
		hay at harvest	<0.005 (16)	<0.005 (16)	<0.005 (16)	<0.005 (16)	<0.005 (16)	
sugar beet	0.19	leaves, green	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	Gaydosh, 1991g
		leaves, at harvest	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	
		roots, at harvest	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	<0.005 (6)	

[1] green forage or green plant 45 days after sowing

Animal transfer studies

Cow feeding study. Groups of three lactating cows were fed quintozene (98.2% PCNB, 0.1% PB, 1.4% HCB) at nominal levels of 0.1, 1 and 10 ppm in the diet for 12-15 weeks. Samples of the milk were taken on days 0, 1, 7, and then at weekly intervals to day 56. Samples of kidneys, muscle and fat were analysed at slaughter, 16 weeks after the start of feeding (Griffith *et al*., 1969).

The LODs of PB, PCA, HCB and quintozene in milk were 0.001, 0.001, 0.005 and 0.01

mg/kg. PCTA could not be quantified because of interference. HCB reached a plateau at about five weeks at 0.014 mg/kg and PCA almost immediately at 0.005 mg/kg in the milk from the cows at the 10 ppm feeding level. The other compounds were detected sporadically at or below the LOD (Table 21).

Table 21. Residues of quintozene, its metabolites and impurities in milk (average of three cows per feeding group).

Days	Residues, mg/kg[1]											
	Feeding level 0.1 ppm				Feeding level 1 ppm				Feeding level 10 ppm			
	PB	HCB	PCNB	PCA	PB	HCB	PCNB	PCA	PB	HCB	PCNB	PCA
0	<0.001	<0.001	<0.01	<0.005	<0.001	<0.001	<0.01	<0.005	<0.001	<0.001	<0.01	<0.005
1	<0.001	<0.001	<0.01	<0.005	<0.001	<0.001	<0.01	<0.005	<0.001	0.002	<0.01	<0.005
7	<0.001	<0.001	<0.01	<0.005	<0.001	<0.001	<0.01	<0.005	<0.001	0.003	<0.01	<0.005
14	<0.001	<0.001	<0.01	<0.005	<0.001	0.001	<0.01	<0.005	<0.001	0.01	<0.01	0.006
21	<0.001	<0.001	<0.01	<0.005	<0.001	0.001	<0.01	<0.005	<0.001	<0.008	<0.01	<0.005
28	<0.001	<0.001	<0.01	<0.005	<0.001	0.002	<0.01	<0.005	<0.001	0.012	<0.01	0.005
35	<0.001	<0.001	<0.01	<0.005	<0.001	0.002	<0.01	<0.005	<0.001	0.031	<0.01	0.005
42	<0.001	<0.001	<0.01	<0.005	<0.001	0.003	<0.01	<0.005	<0.001	0.016	<0.01	0.008
49	<0.001	<0.001	<0.01	<0.005	<0.001	0.001	<0.01	<0.005	<0.001	0.012	<0.01	<0.005
56	<0.001	<0.001	<0.01	<0.005	<0.001	0.003	<0.01	<0.005	<0.001	0.015	<0.01	0.006

[1] PCTA could not be quantified owing to interference

Tissues. The LODs of PB, HCB, quintozene and PCA in tissues are indicated in Table 22 at the 0.1 ppm feeding level. PCTA could not be quantified owing to interference.

In an additional experiment a single cow was fed at 1,000 ppm and slaughtered after one month. PCTA was detected, and could be quantified in the muscle and fat (Table 23).

Table 22. Residues of quintozene, its metabolites and impurities in cow tissues (maximum single values).

Sample	Residues, mg/kg[1]											
	Feeding level 0.1 ppm				Feeding level 1 ppm				Feeding level 10 ppm			
	PB	HCB	PCNB	PCA	PB	HCB	PCNB	PCA	PB	HCB	PCNB	PCA
Kidneys	<0.004	<0.01	<0.05	<0.05	<0.004	<0.01	<0.05	<0.05	<0.004	0.06	<0.05	0.1
Liver	<0.003	<0.02	<0.05	<0.05	<0.003	<0.02	<0.05	<0.05	<0.003	0.11	<0.05	<0.05
Muscle	<0.003	<0.02	<0.05	<0.05	<0.003	<0.02	<0.05	<0.05	0.004	0.11	<0.05	<0.05
Fat, abdominal	<0.008	<0.02	<0.1	<0.08	<0.008	0.1	<0.1	<0.08	<0.008	0.8	<0.1	0.5
Fat, subcutaneous	<0.008	<0.02	<0.1	<0.08	<0.008	0.08	<0.1	<0.08	<0.008	0.7	<0.1	0.38

[1] PCTA could not be quantified

Table 23. Residues of quintozene, its metabolites and impurities in cow tissues after feeding for 1 month with 1000 ppm quintozene in the diet.

Sample	Residues, mg/kg				
	PB	HCB	PCNB	PCA	PCTA
Kidneys	0.005	0.036	<0.05	0.25	<0.08
Liver	0.001	0.093	<0.05	0.029	<0.05
Muscle	0.004	0.095	<0.05	0.089	0.014
Fat, abdominal	0.049	2.3	<0.1	1.2	0.14
Fat, subcutaneous	0.036	1.3	<0.1	1.1	0.075

Chicken feeding study. Chickens were fed with quintozene at levels of 0, 0.05, 1, 5, 15, 75 and 300 ppm in the diet for four months (Griffith and Kuchar, 1975). Eggs, collected each day, and fat, meat and liver were analysed for quintozene, HCB, PB, PCA and PCTA. The LODs are given in Tables 24 and 25.

Residues of PB and HCB became constant in egg yolks at about three weeks and in fat at about seven weeks, whereas quintozene, PCA and PCTA reached equilibrium in less than a week in both egg yolk and fat (Table 24).

Table 24. Residues of quintozene, its metabolites and impurities in chicken egg yolks and fat (average levels at equilibrium).

Feeding level, ppm	Residues in egg yolk, mg/kg					Residues in fat, mg/kg				
	PB	HCB	PCNB	PCA	PCTA	PB	HCB	PCNB	PCA	PCTA
LOD	0.005	0.008	0.01	0.01	0.01	0.006	0.01	0.03	0.02	0.02
0.05	<0.005	<0.008	<0.01	<0.01	<0.01	<0.006	0.05	<0.03	0.04	<0.02
1	<0.005	0.012	<0.01	<0.01	<0.01	0.008	0.06	<0.03	0.03	<0.02
5	<0.005	0.078	<0.01	<0.01	<0.01	0.023	0.36	0.03	0.03	<0.02
15	0.011	0.36	<0.01	0.01	<0.01	0.064	1.4	0.09	0.05	0.02
75	0.072	2.1	0.02	0.08	0.01	0.33	6.7	0.23	0.1	0.04
300	0.22	8.1	0.02	0.17	0.02	1.6	26	1.4	0.28	0.12

Table 25. Residue of quintozene, its metabolites and impurities in chicken egg whites, meat and liver (maximum single values).

Feeding level, ppm	Residues in egg white, mg/kg					Residues in meat, mg/kg					Residues in liver, mg/kg				
	PB	HCB	PCNB	PCA	PCTA	PB	HCB	PCNB	PCA	PCTA	PB	HCB	PCNB	PCA	PCTA
LOD	0.002	0.005	0.01	0.009	0.008	0.01	0.01	0.04	0.04	0.03	0.006	0.01	0.03	0.02	0.02
0.05	<0.002	<0.005	<0.01	<0.009	<0.008	<0.01	<0.01	<0.04	<0.04	<0.03	<0.006	0.017	<0.03	<0.02	<0.02
1	<0.002	<0.005	<0.01	<0.009	<0.008	<0.01	<0.01	<0.04	<0.04	<0.03	<0.006	0.03	<0.03	<0.02	<0.02
5	<0.002	<0.005	<0.01	<0.009	<0.008	<0.01	<0.01	<0.04	<0.04	<0.03	<0.006	0.12	<0.03	<0.02	<0.02
15	<0.002	<0.005	<0.01	<0.009	<0.008	<0.01	<0.01	<0.04	<0.04	<0.03	0.006	0.17	<0.03	<0.02	<0.02
75	<0.002	<0.005	<0.01	<0.009	<0.008	<0.01	0.05	<0.04	<0.04	<0.03	0.04	1.02	<0.03	<0.02	<0.02
300	<0.002	0.02	0.01	0.01	<0.008	0.03	0.7	<0.04	<0.04	<0.03	0.24	6.6	<0.03	<0.02	0.17

FATE OF RESIDUES IN STORAGE AND PROCESSING

In storage

No data were received.

In processing

Processing studies were conducted on tomatoes and potatoes. Data on residues in processed cotton seed and peanuts were also provided (Ball, 1989c, 1990f) but the studies were not accepted by the US EPA. No current data were received.

Tomatoes. For the processing study tomatoes were treated with a WP formulation at 42 kg ai/ha, 5 times the maximum label rate. After washing, the tomatoes were fed through a disintegrator and then heated. The hot tomato juice (106°C) was passed through a finisher to remove skins and seeds and collected to produce canned juice and concentrate. Canned juice: some of the juice was filled into cans which were sealed and cooked for an additional 10 minutes in boiling water to ensure sterility before cooling. Concentrate: the remaining hot juice from each lot was concentrated, then filled in cans, sealed and cooked for 30 min in boiling water before cooling.

The wet pomace (skins and seeds) from the concentrator was weighed and divided into two equal lots, one of which was dried in a hot-air dehydrator at 66°C.

To produce whole-pack tomatoes the tomatoes were blanched in boiling water to remove the skins, then canned and covered with juice from the corresponding lots. The cans were then vacuum-sealed and cooked for 30 min in a rotary cooker before cooling.

The results are shown in Table 26 (Ball, 1990c). Samples of all the processed products except dry pomace were re-analysed (Ball, 1990d) by a modified analytical method with an LOD of 0.002 mg/kg.

Table 26. Residues of quintozene, its metabolites and impurities in processed products of tomatoes treated with single applications of WP at 42 kg ai/ha, USA, 1990.

Sample	Residues, mg/kg					Ref.
	PCNB	PB	HCB	PCTA	PCA	
Tomato[1], unwashed	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	Ball, 1990c
Tomato, washed	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	
Canned tomato	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	
Tomato juice	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	
Tomato ketchup	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	
Tomato purée	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	
Tomato paste	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	<0.05 (4)	
Pomace, dry	0.13 0.14 0.14 0.14 0.15 <0.05 0.17 0.2	<0.05 (8)	<0.05 (8)	<0.05 (8)	0.08 0.09 0.08 <0.05 0.1 <0.05 0.08 <0.05	

Sample	Residues, mg/kg					Ref.
	PCNB	PB	HCB	PCTA	PCA	
Pomace, wet	0.06 (3) 0.07 (2) 0.08 (2) 0.09	<0.05 (7) 0.05	<0.05 (8)	<0.05 (8)	<0.05 (8)	
Re-analysed						Ball, 1990d
Tomato,[1] unwashed	<0.002 0.003	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	
Tomato, washed	0.002 0.007	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 0.003	
Canned tomato	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	
Tomato juice	<0.002 (3)	<0.002 (3)	<0.002 (3)	<0.002 (3)	<0.002 (3)	
Tomato ketchup	<0.002 (3)	<0.002 (3)	<0.002 (3)	<0.002 (3)	<0.002 (3)	
Tomato purée	<0.002 (2)	<0.002 (2)	<0.002 (2)	<0.002 (2)	0.003 <0.002	
Tomato paste	<0.002 (3)	<0.002 (3)	<0.002 (3)	<0.002 (3)	0.003 <0.002	
Pomace, wet	0.047 0.044	<0.002 (2)	<0.002 (2)	<0.002 0.003	0.015 0.013	

[1] PHI 111-124 days

Potatoes. For the processing study, potatoes were treated with two, four, five or ten times the maximum label rate.

To produce chips unpeeled potatoes were washed, sliced and fried in maize oil for 2.5 to 2.8 min at 185°C to a final moisture content of approximately 2%. For flakes and granules the potatoes were lightly peeled in a peeler for 45 sec. The slices were washed and cooked with steam at 99°C for 20 min. A smooth, uniform slurry was prepared, which was used for the production of both flakes and granules. For flakes, a portion of the slurry was dried in a thin layer at 49°C to a final moisture content of 5-6%. To produce granules the slurry was homogenized and pumped into a mixed flow spray drier (149°C). The final moisture content was approximately 4-6%. The results are shown in Table 27 (Ball, 1987).

Table 27. Residues of quintozene, its metabolites and impurities in processing products of potatoes, USA 1967. All single applications (Ball, 1987).

Form, method	kg, ai/ha	Sample	Residues, mg/kg				
			PCNB	PB	HCB	PCTA	PCA
GR in-furrow	56	tuber[1], raw, whole	0.085 0.086	0.02 0.034	0.005 0.013	0.014 0.04	0.002 0.077
		chips, raw	0.080 0.12	0.01 0.017	0.005 0.007	0.012 0.024	0.017 0.037
		chips, cooked	0.04 0.068	0.005 0.01	0.002 0.005	0.008 0.03	0.005 0.012
		slurry	0.003 (2)	0.006 0.009	<0.002 0.004	<0.002 0.003	0.005 0.017
		flakes	0.005 0.009	0.004 0.012	0.003 0.01	0.003 0.01	0.005 0.042
		granules	0.004 <0.002	0.004 <0.002	0.007 0.002	0.007 <0.002	0.041 0.013
GR in-furrow	112	tuber,[1] raw, whole	0.12 0.28	0.029 0.037	0.010 0.009	0.033 0.025	0.061 0.047
		chips, raw	0.061 0.33	0.012 0.015	0.004 0.006	0.015 0.020	0.030 0.029
		chips, cooked	0.12 0.046	0.017 0.003	0.007 0.002	0.048 0.009	0.026 0.002
		slurry	<0.002 0.009	0.006 0.012	0.003 (2)	0.002 0.003	0.013 0.011
		flakes	0.005 0.016	0.004 0.008	0.010 0.004	0.005 0.006	0.038 0.009
		granules	<0.002 0.002	<0.002 (2)	<0.002 0.004	<0.002 0.002	0.013 0.014
EC broadcast	140	tuber,[1] raw, whole	0.11 0.61	0.072 0.053	0.019 0.014	0.059 0.047	0.13 0.064
		chips, raw	0.11 0.62	0.052 0.033	0.015 0.011	0.050 0.042	0.11 0.053
		chips, cooked	0.15 0.14	0.036 0.011	0.017 0.003	0.094 0.021	0.024 0.009
		slurry	0.002 0.019	0.019 0.018	0.006 0.005	0.004 0.007	0.030 0.015
		flakes	0.008	0.025	0.013	0.015	0.073

Form, method	kg, ai/ha	Sample	Residues, mg/kg				
			PCNB	PB	HCB	PCTA	PCA
			0.025	0.010	0.007	0.009	0.012
		granules	<0.002 0.002	0.004 <0.002	0.006 0.009	0.007 0.002	0.047 0.018
EC broad-cast	280	tuber,[1] raw, whole	0.25 0.99	0.083 0.064	0.029 0.018	0.084 0.054	0.16 0.070
		chips, raw	0.46 0.72	0.099 0.019	0.040 0.008	0.16 0.025	0.22 0.031
		chips, cooked	0.44 0.13	0.054 0.009	0.027 0.005	0.16 0.028	0.053 0.011
		slurry	0.006 0.016	0.030 0.012	0.013 0.003	0.012 0.005	0.054 0.009
		flakes	0.022 0.024	0.046 0.009	0.029 0.008	0.039 0.007	0.12 0.015
		granules	0.006 0.003	0.013 <0.002	0.011 0.007	0.018 <0.002	0.090 0.013

[1] PHI 133-139 days

Residue in the edible portion of food commodities

Beans. Mean residues in snap beans and bean cannery waste (culls, leaves, stems) found in three studies are shown in Table 28. Residues of the five compounds (quintozene, PB, HCB, PCA and PCTA) in the whole beans and the waste were similar. The slight increase in PB, HCB and PCA in the waste (1.2 to 1.5 times) is of little significance at these levels (Ball, 1990e).

Table 28. Average residues in beans and bean cannery waste.

Sample	No.	Residues, mg/kg				
		PCNB	PB	HCB	PCTA	PCA
Seed with pods	3	0.11	<0.002	0.003	0.016	0.12
Pods no tip	2	0.089	<0.002	0.003	0.019	0.14
Cannery waste	3	0.097	0.003	0.004	0.016	0.14

Other commodities. No data were received except those recorded in Tables 12 (cabbages with and without wrapper leaves), 19 (peanuts) and 20 (cereal grains, peas).

RESIDUES IN FOOD IN COMMERCE OR AT CONSUMPTION

No data were received.

NATIONAL MAXIMUM RESIDUE LIMITS

The following national MRLs were reported.

Definition of the residue

quintozene

Australia, Canada, Germany, USA: quintozene

The Netherlands: quintozene including pentachloroaniline and pentachlorothioanisole, expressed as sum of quintozene, pentachloroaniline and pentachlorothioanisole.

Country	Commodity	MRL, mg/kg
Australia	banana	1
	beans, except broad beans and soya beans	0.01
	broad beans (green pods and immature seeds)	0.01
	brassica vegetables (cole or cabbage)	0.02
	common beans (dry)	0.2
	cotton seed	0.03
	lettuce, head	0.3
	lettuce, leaf	0.3
	mushrooms	10
	onion, bulb	0.2
	peanuts	0.3
	peppers, sweet	0.01
	potatoes	0.2
	tomatoes	0.1
Canada	beets	0.1
Germany	banana	1
	brassica vegetables	0.02
	lettuce and similar	0.3
	witloof	0.3
	other plant commodities	0.01
The Netherlands	banana	1
	brassicas, head	0.02
	broccoli	0.02
	cotton seed	0.03
	legume vegetables	0.01[1]
	lettuce, head	3
	peanuts	2
	peppers	0.01[1]
	potatoes	0.2[1]
	pulses	0.2[1]
	purslane	0.1[2]
	tomatoes	0.1
	radish	0.5[2]
	other food commodities	0.01*
USA	beans	0.1 (I)
	broccoli	0.1 (I)
	brussels sprouts	0.1 (I)

quintozene

Country	Commodity	MRL, mg/kg
	cabbage	0.1 (I)
	cauliflower	0.1 (I)
	collards (Georgia)	0.2 (R)
	cotton seed	0.1 (N)
	garlic	0.1 (I)
	kale (Georgia)	0.2 (R)
	mustard greens (Georgia)	0.2 (R)
	peanut	1 (I)
	peppers	0.1 (I)
	potato	0.1 (I)
	tomatoes	0.1 (I)

* limit of determination (LOD)
[1] under consideration
[2] under consideration for withdrawal
(I) interim tolerance
(N) negligible residue tolerance
(R) regional tolerance

APPRAISAL

Quintozene, originally evaluated by the JMPR in 1969 and re-evaluated for residues several times up to 1977, is included in the CCPR periodic review programme. The 1991 CCPR scheduled the periodic review for 1995 because new data were reported to be available (ALINORM 91/24A, para 316 and Appendix VI, para 15).

The Meeting received studies of animal and plant metabolism, analytical methods, updated information on GAP, data from supervised residue trials on vegetables and oilseed, and information on residues after storage and processing from the manufacturer. Information on analytical methods and national MRLs was also made available by The Netherlands, and on GAP by Australia, Canada and the UK. Germany and The Netherlands do not have registered uses.

The metabolism of quintozene was investigated in rats, goats, and chickens. In general, the metabolic pathways in all these species were similar. The major routes were (1) displacement of the nitro group by the sulfhydryl group of reduced glutathione or SH-containing amino acids and peptides, or by hydroxyl to yield pentachlorophenol; (2) reduction of the nitro group to form *N*-hydroxypentachloroaniline and conjugated pentachloroaniline; (3) dechlorination to yield tetrachloro analogues of the above compounds.

A feeding study on goats showed that quintozene was converted mainly to pentachloroaniline (PCA) and its glucuronide conjugate. Other metabolites formed in much smaller amounts were tetrachlorothioanisole, pentachlorothiophenol, and methyl tetrachlorophenyl sulfoxide. The majority of the activity was eliminated in the urine and faeces (38.3% and 19.2% respectively). Milk and fat contained only one metabolite, identified as PCA. No quintozene was detected in the tissues, milk or urine.

When quintozene was fed to laying hens, pentachlorothioanisole (methyl pentachlorophenyl sulfide, PCTA), pentachlorothiophenol and pentachlorothiophenol conjugates with cysteine, malonylcysteine, pyruvate and acetate were identified in various tissues, eggs and excreta. Other metabolites found included tetrachlorothioanisole, tetrachlorothioanisole sulfone, pentachlorothioanisole sulfoxide and tetrachloromethylsulfinylaniline ("methyl tetrachloroaniline sulfoxide"). A second pathway involved reduction of the nitro group to produce pentachloroaniline and *N*-hydroxypentachloroaniline.

Metabolism studies in plants (cabbage, potato and peanut) showed three major pathways similar to those in animals: reduction of the nitro group to form *N*-hydroxypentachloroaniline and pentachloroaniline, displacement of the nitro group by the sulfhydryl group of glutathione to give a glutathione adduct which is metabolized further or, to a lesser extent, by a hydroxyl group to give pentachlorophenol, and reductive or oxidative dechlorination, replacing chlorine by hydrogen or hydroxyl.

In cabbages grown in soil treated with [^{14}C]quintozene, the highest levels of radioactivity were found in the outer leaves. Seven metabolites were identified in leaf extracts, the two major ones being methyl tetrachlorophenyl sulfoxide and sulfone. Five minor components were identified as a methyl trichlorophenol sulfone, *N*-hydroxylated pentachloroaniline, methyl pentachlorophenyl sulfoxide and pentachlorothioanisole.

In potatoes grown in soil treated with [^{14}C]quintozene applied by pre-plant incorporation, only 6.4% of the total radioactivity was located in the potato pulp and 94% in the peel. The chloroform-soluble substances were identified mainly as pentachloronitrobenzene and pentachloroaniline with lesser amounts of pentachlorothioanisole, tetrachloronitrobenzene, tetrachlorophenol, and *N*-hydroxypentachloroaniline. Ether- and water-soluble residues were mainly conjugates of pentachlorothiophenol.

In peanuts planted in soil treated with [^{14}C]quintozene, the highest levels of ^{14}C were found in the roots (97%). The vines, shells and nuts had residues ranging from 2.7% in vines to 0.3% in nuts. Extraction with aqueous methanol removed 64-88% of the ^{14}C. The extract contained seven metabolites. The two major metabolites were identified as *S*-pentachlorothiophenyl-2-*N*-malonylcysteine and tetrachloroaniline, which were found in the roots, vines and shells.

No information on environmental fate was received. For this reason the Meeting recommended the withdrawal of all existing MRLs.

For residue analysis samples are extracted with hexane and cleaned up by liquid-liquid partition, GPC and Florisil column chromatography. Determination is by GLC with electron-capture detection. Limits of determination for quintozene, hexachlorobenzene (HCB), pentachlorobenzene (PB), pentachlorothioanisole (PCTA) and pentachloroaniline (PCA) in vegetables, nuts, oilseeds, milk, animal tissues and eggs ranged from 0.0005 to 0.05 mg/kg, and recoveries from 86 to 104% at fortification levels from 0.025 to 0.2 mg/kg.

The Meeting considered differences between the analytical conditions in specified laboratories and concluded that 0.01 or 0.05 mg/kg, depending on the commodity, were practical limits of determination of the parent compound for enforcement. For risk assessment purposes the Meeting noted that the total residues were relevant.

The residue was defined by a former JMPR as the sum of quintozene, PCTA and PCA. The present Meeting considered that the residue definition for risk assessment purposes for plant and animal commodities should be the sum of quintozene, PCTA and PCA, expressed as quintozene. This definition is also suitable for animal commodities for enforcement purposes since the parent quintozene is not an appropriate indicator compound for such commodities. Quintozene alone is a suitable definition of the residue for enforcement purposes for crops. On the basis of the metabolism and animal transfer studies the Meeting agreed that quintozene should be described as fat-soluble. The rationale for the definition of residues is given in Section 2.8.1 of this report.

Studies of the stability of stored analytical samples showed that quintozene and its metabolites or impurities are stable as residues in head cabbages, kidney beans, potatoes, wheat, cotton seed and peanuts when stored at -20°C up to one year. Residues decreased to approximately 60-70% of the initial levels in peppers, tomatoes (including processed products), maize and soya beans after storage for six to eight months.

quintozene

Quintozene is applied to garlic, beans, other vegetable seeds, potatoes, cereals and oilseed as a single seed treatment with DS, EC, FS, LS, PS or WP formulations, and to bulb, brassica, fruiting, leafy, legume, root and tuber vegetables, pulses, oilseed and coffee beans as one or two soil or plant treatments before or at planting with EC, DP, GR, SC or WP. The PHI depends on local conditions and is not relevant where the application is before or at the time of planting.

Primary food commodities of plant origin

The Meeting reviewed data on US supervised residue trials involving soil or plant treatments of broccoli, head cabbages, peppers, tomatoes, beans, potatoes, cotton seed and peanuts, and seed treatments of sugar beet, peas, barley, maize and soya beans. Residues of quintozene, the metabolites PCTA and PCA, and the impurities HCB and PB were detected.

In the calculation of the total residues, the molecular weights of quintozene (295) and PCTA (296) are effectively the same. The molecular weight of PCA is 265 and a factor of 1.1 is used to express PCA as quintozene. Where concentrations of the individual metabolite PCA are given below these have been corrected by this factor and are therefore expressed as quintozene.

Bananas. No residue data were available. The Meeting was informed that quintozene was not used on bananas and agreed to withdraw the previous recommendation of 1 mg/kg.

Broccoli, Head cabbages. The US residue trials were according to US GAP for brassica vegetables (max. 34 kg ai/ha soil treatment broadcast) and approximately according to Australian GAP (37-56 kg ai/ha).

Broccoli plants were harvested at maturity, at PHIs of 64-83 days. 48 samples were analysed with a maximum total residue of 0.094 mg/kg (0.05 mg/kg quintozene, 0.044 mg/kg PCA, 0.004 mg/kg PCTA). PB and HCB could not be determined (<0.002 mg/kg). On the basis of these data the Meeting estimated maximum residue levels of 0.1 mg/kg total residue and 0.05 mg/kg parent compound to replace the previous recommendation (0.02 mg/kg).

In the cabbage trials plants were grown to maturity and harvested 67-125 days after application. 70 samples of white and savoy cabbage were analysed. In the samples without wrapper leaves the maximum total residue was 0.02 mg/kg (0.016 mg/kg quintozene, <0.002 mg/kg PCA and PCTA) and the residues of the impurities PB and HCB <0.002 mg/kg. In the samples with wrapper leaves, the maximum total residue was 0.11 mg/kg (0.062 mg/kg quintozene, 0.045 mg/kg PCA, 0.006 mg/kg PCTA) and the residues of the impurities 0.003 mg/kg PB and <0.002 mg/kg HCB. The Meeting estimated maximum residue levels of 0.2 mg/kg total residue and 0.1 mg/kg parent compound for head cabbages, based on the residues in samples with wrapper leaves, to replace the previous recommendation (0.02 mg/kg).

Other brassica vegetables. Quintozene is registered for soil treatment in Australia, the UK and the USA for brassica vegetables and in New Zealand for vegetables, but residue data were not available. The Meeting agreed that residue data from head brassicas and broccoli could not be extrapolated to cauliflower, Brussels sprouts or kohlrabi. A maximum residue level could not be estimated.

Sweet peppers, Tomatoes. The US residue trials were in accord with US GAP (max. 8.4 kg ai/ha).

In the trials on peppers the plants were harvested at maturity, at PHIs of 71-104 days. In the 20 samples analysed, the residues of quintozene, PB, HCB, PCA and PCTA were below the limits of determination (<0.05 mg/kg). The Meeting estimated maximum residue levels of 0.2* mg/kg total residue and 0.05* mg/kg parent compound as being practical limits of determination to replace the previous recommendation (0.01 mg/kg).

In the trials on tomatoes the fruits were harvested at maturity, at PHIs of 73-113 days. In the 18 samples analysed the maximum total residue was 0.016 mg/kg (0.012 mg/kg quintozene, <0.002 mg/kg PCA and PCTA). PB and HCB were below the limit of determination of 0.002 mg/kg. The Meeting estimated a maximum residue level of 0.02 mg/kg (both the total residue and parent compound), to replace the previous recommendation (0.1 mg/kg).

Head lettuce. The use of quintozene on lettuce is registered in Australia as a soil application at singling, with a maximum of 0.11 kg ai/hl, and in New Zealand under the general GAP for vegetables. No residue data were received. The Meeting was informed that new studies were being considered but agreed to withdraw the recommendation of 3 mg/kg.

Common beans (pods and/or immature seeds), Common beans (dry). The trials at three US test locations (with treatment with three different formulations on each site) were in accordance with US GAP (1 soil treatment at max. 1.7 kg ai/ha).

Fresh beans were harvested at maturity, at PHIs of 42 to 62 days. In the samples analysed (from 18 trials) the maximum total residue was 0.093 mg/kg (0.081 mg/kg quintozene, 0.011 mg/kg PCA, <0.0005 mg/kg PCTA). PB and HCB were below the limit of determination (0.0005 mg/kg). In addition, 26 results from trials at exaggerated application rates were received. On the basis of the GAP trials, the Meeting estimated a maximum residue level of 0.1 mg/kg (both the total residue and parent compound) to replace the previous recommendation (0.01 mg/kg).

In the 18 trials on dry beans the beans were harvested at maturity, at PHIs of 77 to 106 days. 18 samples were analysed with a maximum total residue of 0.03 mg/kg (0.02 mg/kg quintozene, 0.008 mg/kg PCA, 0.002 mg/kg PCTA). PB and HCB were below the limit of determination of 0.0005 mg/kg. Results of 19 trials at exaggerated rates were also received. On the basis of the GAP trials, the Meeting estimated maximum residue levels of 0.03 mg/kg total residue and 0.02 mg/kg parent compound for common beans (dry) to replace the previous recommendation (0.2 mg/kg).

Peas (dry). Results of eight US seed treatment trials on peas (0.12 kg ai/100 kg seed) were received, approximately in accordance with US GAP (0.096 kg ai/100 kg seed). The maximum total residue in dried peas was 0.017 mg/kg (0.007 mg/kg quintozene, <0.005 mg/kg PCA and PCTA). The Meeting estimated maximum residue levels of 0.02 mg/kg total residue and 0.01 mg/kg parent compound for dry peas.

Soya beans (dry). Sixteen US seed treatment trials on soya beans (0.1 kg ai/100 kg seed) approximated US GAP (0.096 kg ai/100 kg seed). No residues of quintozene, PB, HCB, PCA or PCTA were found above the LOD of 0.005 mg/kg in the beans at harvest. The Meeting estimated maximum residue levels of 0.02* mg/kg total residue and 0.01* mg/kg parent compound for soya beans (dry) as being practical limits of determination.

Potatoes. Quintozene is registered in Australia, Cyprus, Israel, Saudi Arabia and South Africa, but no residue data were received. US residue results based on single applications of 28 kg ai/ha (broadcast, 28 values) and 11 to 13 kg ai/ha (in-furrow, 22 values) were provided. The potatoes were harvested at maturity, at PHIs of 82 to 135 days. The maximum total residue was 1.5 mg/kg (0.96 mg/kg quintozene, 0.28 mg/kg PCA, 0.24 mg/kg PCTA). In the same sample, 0.064 mg/kg PB and 0.033 mg/kg HCB were determined. The Meeting was informed that new studies were being considered but concluded that as the US residue data could not be related to reported GAP it could not estimate a maximum residue level and agreed to withdraw the previous recommendation of 0.2 mg/kg.

Sugar beet. In eight US seed treatment trials according to GAP (0.19 kg ai/100 kg seed) no residues of quintozene were found above the LOD of 0.005 mg/kg in green leaves, or in roots or leaves at harvest. The Meeting estimated maximum residue levels of 0.02* mg/kg total residue and 0.01* mg/kg parent compound for sugar beet as being practical limits of determination.

Barley. Six US seed treatment trials on barley (0.13 kg ai/100 kg seed) showed no residues of quintozene, PB, HCB, PCA and PCTA above the LOD of 0.005 mg/kg in the grain. The trials were approximately in accord with GAP in Spain (0.04-0.2 kg ai/100 kg seed) and the USA (max. 0.11 kg ai/100 kg seed). The Meeting estimated maximum residue levels of 0.02* mg/kg total residue and 0.01* mg/kg parent compound for barley as being practical limits of determination.

Maize. In 12 US seed treatment trials on maize (0.052 kg ai/100 kg seed) no residues of quintozene, PB, HCB, PCA and PCTA were found above the LOD of 0.005 mg/kg in the grain. The trials accorded approximately with GAP in Spain (0.04-0.2 kg ai/100 kg seed) and the USA (0.048 kg ai/100 kg seed). The Meeting estimated maximum residue levels of 0.02* mg/kg total residue and 0.01* mg/kg parent compound for maize as being practical limits of determination.

Wheat. Seed treatment with quintozene is registered in Brazil at 0.19 kg ai/100 kg seed and in the USA at 0.048 kg ai/100 kg seed. 20 US seed treatment trials at an application rate of 0.052 kg ai/100 kg seed showed a maximum total residue of 0.016 mg/kg (0.0061 mg/kg quintozene, <0.005 mg/kg PCA and PCTA) in the grain. No residues of PB or HCB were found above the LOD of 0.005 mg/kg. The Meeting estimated maximum residue levels of 0.02 mg/kg total residue and 0.01 mg/kg parent compound.

Cotton seed. The available US trials were in accordance with US GAP (1 soil treatment in-furrow at planting, maximum 2.3 kg ai/ha). Cotton seed was harvested at maturity, approximately five months after treatment. 36 samples were analysed with a maximum total residue of 0.028 mg/kg (0.008 mg/kg quintozene, 0.015 mg/kg PCA, <0.005 mg/kg PCTA). No residues of PB or HCB (<0.002, <0.005 mg/kg) were found. The Meeting estimated the previous MRL of 0.03 mg/kg as the total maximum residue level and estimated a maximum residue level of 0.01 mg/kg for the parent compound.

Peanuts. The available US trials approximated US GAP (maximum 2 soil applications of 5.6 kg ai/ha). Peanuts were harvested at maturity, 45 to 47 days after the last treatment. 32 samples of peanut kernels and hulls were analysed. In the hulls the maximum total residue was 1.3 mg/kg (0.94 mg/kg quintozene, 0.18 mg/kg PCA, 0.19 mg/kg PCTA). The same sample showed residues of 0.032 mg/kg PB and 0.013 mg/kg HCB. In the kernels the maximum total residue in any one sample was 0.45 mg/kg (0.15 mg/kg quintozene, 0.18 mg/kg PCA, 0.12 mg/kg PCTA). The same sample contained 0.046 mg/kg PB and 0.017 mg/kg HCB. The maximum residue of the parent quintozene was 0.25 mg/kg, found in another sample (0.077 mg/kg PCA, 0.04 mg/kg PCTA, 0.045 mg/kg PB, 0.006 mg/kg HCB). No results were available for whole peanuts. The Meeting estimated a maximum residue level of 0.5 mg/kg (both total residue and parent compound) for peanuts to replace the previous recommendation (2 mg/kg), and agreed to withdraw the previous recommendation for whole peanuts of 5 mg/kg.

Animal products

Cattle. The Meeting reviewed a feeding study on dairy cows in which quintozene was fed at levels of 0.1, 1 and 10 ppm for 12-15 weeks. In the samples from the 0.1 and 1 ppm levels, no residues were found above the LOD of quintozene, PB or PCA in milk (<0.01, <0.001 and <0.005 mg/kg), kidneys, liver, muscle (<0.05 mg/kg quintozene and PCA, <0.004 mg/kg PB), or fat (<0.1, <0.008 and 0.08 mg/kg). PCTA could not be quantified. Only HCB was detected in milk at the 1 ppm feeding level, with maximum residues at days 28-56 of 0.002-0-003 mg/kg. No HCB above the LOD of 0.02 mg/kg was found in the tissues, but fat showed a maximum residue of 0.1 mg/kg. Because PCTA was not analysed and the residue is defined as the sum of quintozene, PCA and PCTA the results are insufficient to estimate maximum residue levels for milk, meat or other edible products of cattle.

Chickens. Chickens were fed quintozene at levels of 0.05, 1, 5, 15, 75 and 300 ppm in the diet for four months. No residues of quintozene, PCA or PCTA were found above the LODs of 0.01 mg/kg in egg yolk and white, 0.04 mg/kg in meat and 0.03 mg/kg in liver, in the 0.05, 1, 5 or 15 ppm groups. In fat, no quintozene residues above 0.04 mg/kg could be found at levels up to 5 ppm. PB could not be found up to the 1 ppm feeding level in egg yolk (<0.005 mg/kg), egg white (<0.002 mg/kg), meat (<0.01 mg/kg) or liver (<0.006 mg/kg); 0.008 mg/kg was found in fat. HCB was determined in the 0.05 ppm group in fat (0.05 mg/kg) and liver (0.017 mg/kg) and in the 1 ppm group in egg yolk, fat and liver (0.012, 0.06 and 0.03 mg/kg), but not in egg white (<0.005 mg/kg) or meat (<0.01 mg/kg). No residues would be expected in practice from the use of quintozene, because the estimated maximum residue levels (both total and parent) in potential feeding-stuffs are generally less than 0.5 mg/kg. On the basis of the feeding levels up to 5 ppm and a maximum residue of 0.5 mg/kg to be expected in the diet, the Meeting estimated maximum total residue levels of 0.03* mg/kg for eggs and 0.1* mg/kg for chicken meat and edible offal as practical limits of determination.

Cereal fodders and straws

US seed treatment trials on barley, maize and wheat are described above, with details of the relevant GAP. Residues in the animal feed commodities were evaluated as follows.

Barley straw and fodder, dry. Four US trials on barley showed no residues of quintozene, PB, HCB, PCA or PCTA above the LOD of 0.005 mg/kg in barley straw. The Meeting estimated maximum residue levels of 0.02* mg/kg total residue and 0.01* mg/kg parent compound as being practical limits of determination for barley straw and fodder, dry.

Maize forage and fodder. Thirteen results were received. No residues of quintozene, PB, HCB, PCA or PCTA were found above the LOD of 0.005 mg/kg in maize forage or fodder, except one residue of 0.006 mg/kg quintozene in the fodder. The Meeting estimated maximum residue levels of 0.02* mg/kg total residue and 0.01* mg/kg parent compound as being practical limits of determination for maize forage, and of 0.02 mg/kg (total residue) and 0.01 mg/kg (parent compound) for maize fodder.

Pea hay (dry). Results of eight US seed treatment trials on peas (0.12 kg ai/100 kg seed) were received, which were approximately according to US GAP (0.096 kg ai/100 kg seed). Quintozene residues were found in dried pea hay at <0.005 (4), 0.013, 0.015, 0.016 and 0.02 mg/kg. The Meeting estimated a maximum residue level of 0.05 mg/kg as parent compound for pea hay (dry), based on the rather small database, with four of the eight results at or about 0.02 mg/kg of the parent quintozene. The maximum total residue was 0.042 mg/kg (0.02 mg/kg quintozene, 0.017 mg/kg PCA, <0.005 mg/kg PCTA). PB and HCB could not be determined above the LOD of 0.005 mg/kg. The Meeting estimated a maximum total residue level, also of 0.05 mg/kg.

Soya bean fodder and forage. Sixteen US seed treatment trials on soya beans (0.1 kg ai/100 kg seed) were approximately in accord with US GAP (0.096 kg ai/100 kg seed). In whole green plants no residues of quintozene, PB, HCB, PCA or PCTA were found above the LOD of 0.005 mg/kg. The Meeting estimated maximum residue levels for soya bean forage of 0.02* mg/kg total residue and 0.01* mg/kg parent compound for soya bean forage as being practical limits of determination.

No residues of quintozene, PB, HCB, PCA or PCTA were found above the LOD of 0.005 mg/kg in hay or the whole plant at harvest (except one PCA residue of 0.015 mg/kg expressed as quintozene). The maximum total residue in the fodder was calculated as 0.025 mg/kg (0.015 mg/kg PCA, <0.005 mg/kg quintozene and PCTA). The Meeting estimated maximum residue levels for soya bean fodder of 0.03 mg/kg total residue and 0.01* mg/kg parent compound.

Wheat straw and fodder, dry. 20 trials on wheat showed a maximum total residue in straw of 0.033 mg/kg (0.023 mg/kg quintozene, <0.005 mg/kg PCA and PCTA). There were no residues of PB or HCB (except 1 of 0.014 mg/kg) in any sample. The Meeting estimated maximum residue levels of 0.05 mg/kg total residue and 0.03 mg/kg parent compound.

Processing studies were conducted on tomatoes and potatoes. Processing data on cotton seed and peanuts were also provided, but not evaluated because the validity of the studies was called into question.

Tomatoes were treated at 42 kg ai/ha (5 times the maximum label rate), but residues were too low to show the effects of processing. The study is being repeated.

Potatoes were treated with two, five or ten times the maximum label rate. Residues in the processed potato chips, granules and flakes did not exceed those in the whole raw potatoes (tubers or sliced raw chips). In only two of the eight trials, quintozene residues in cooked potato chips were higher than in the raw commodity. The results indicate that quintozene and its metabolites and impurities would not be concentrated by processing.

Because of the lack of critical supporting data on environmental fate the Meeting could not recommend the maximum residue levels it estimated for use as MRLs and, as mentioned above, recommended the withdrawal of existing MRLs.

Any future reconsideration of recommendations for MRLs will require the submission of data on bioaccumulation and soil degradation and metabolism. Processing studies on tomatoes, cotton seed and peanuts will also be required. Details of the data required are given in the Report of the Meeting, Section 2.5.2.

RECOMMENDATIONS

1. In the absence of critical supporting studies for periodic review the withdrawal of the Codex MRLs listed below is recommended.

Commodity		Existing CXL, mg/kg
CCN	Name	
FI 0327	Banana[1]	1
VB 0400	Broccoli	0.02
VB 0041	Cabbages, Head	0.02
VP 0526	Common beans (pods and/or immature seeds)	0.01
VD 0526	Common beans (dry)	0.2
SO 0691	Cotton seed	0.03

quintozene

Commodity		Existing CXL, mg/kg
CCN	Name	
VL 0482	Lettuce, Head[1]	3
SO 0697	Peanut	2
SO 0703	Peanut, whole	5
VO 0445	Peppers, Sweet	0.01
VR 0589	Potato[1]	0.2
VO 0448	Tomato	0.1

[1] CXLs for banana, lettuce and potatoes are also recommended for withdrawal because uses have been discontinued and/or no residue data were available.

2. The Meeting estimated the maximum residue levels listed below, but these levels are **not** recommended for use as MRLs because critical supporting studies were not provided.

Definitions of the residue

(1) For enforcement purposes for plant commodities: quintozene (fat-soluble).
(2) For enforcement purposes for animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene (fat-soluble).
(3) For risk assessment purposes for plant and animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene (fat-soluble).

Commodity		Estimated max. res. level		PHI on which based, days	Existing CXL
CCN	Name	Parent	Total		
GC 0640	Barley	0.01*	0.02*		
AS 0640	Barley straw and fodder, dry	0.01*	0.02*		
VB 0400	Broccoli	0.05	0.1	64-83	0.02
VB 0041	Cabbages, Head	0.1	0.2	67-125	0.02
PO 0840	Chicken, Edible offal of	0.05*	0.1*		
PM 0840	Chicken meat	0.05*(fat)	0.1*(fat)		
VP 0526	Common beans (pods and/or immature seeds)	0.1	0.1	42-62	0.01
VD 0526	Common beans (dry)	0.02	0.03	77-106	0.2
SO 0691	Cotton seed	0.01	0.03	140-166	0.03
PE 0112	Eggs	0.01*	0.03*		
GC 0645	Maize	0.01*	0.02*		
AS 0645	Maize fodder	0.01	0.02		
AF 0645	Maize forage	0.01*	0.02*		
SO 0697	Peanut	0.5	0.5	45- 47	2
VD 0072	Peas (dry)	0.01	0.02		
AL 0072	Pea hay (dry)	0.05	0.05		
VO 0445	Peppers, Sweet	0.05*	0.2*	71-104	0.001
VD 0541	Soya beans (dry)	0.01*	0.02*		
AL 0541	Soya bean fodder	0.01*	0.03		
AL 1265	Soya bean forage	0.01*	0.02*		
VR 0596	Sugar beet	0.01*	0.02*		
VO 0448	Tomato	0.02	0.02	73-113	0.1

Commodity		Estimated max. res. level		PHI on which based, days	Existing CXL
CCN	Name	Parent	Total		
GC 0654	Wheat	0.01	0.02		
AS 0654	Wheat straw and fodder, dry	0.03	0.05		

REFERENCES

Adamovics, J.A. 1980. The metabolic fate of pentachloronitrobenzene - pilot study. Report No. 79056. Olin Corp. (Volume 3). Unpublished.

Anon. 1988. Multi-residue method 1, submethods 1 and 2, p. 3-7; Analytical methods for residues of pesticides, 5th edition, Ministry of Welfare, Health and Cultural Affairs, Rijswijk, The Netherlands. SDU Publishers, The Hague, The Netherlands; ISBN 90 12 06712 5.

Anon. 1990. Council Directive of 15 October 1990 amending the Annex to the Directive 79/117/EEC prohibiting the placing on the market and use of plant protection products containing certain active substances (90/533/EEC).

Anon. 1994a. Information of the Netherlands on pesticides to be considered by the JMPR 1995 - quintozene. Ministrie van Volksgezondheid, Welzijn en Sport Netherlands, August, 1994. Unpublished.

Anon. 1994b. Information on GAP of quintozene for the 1995 JMPR by Pesticides Safety Directorate United Kingdom, November 31, 1994. Unpublished.

Anon. 1995a. Information on GAP and national MRLs of quintozene for the 1995 JMPR by Agricultural and Veterinary Chemicals Policy Section of Department of Primary Industries and Energy, Australia, May 18, 1995. Unpublished.

Anon. 1995b. Information on GAP and national MRLs of quintozene for the 1995 JMPR by Agriculture and Agri-Food Canada, Food Production andInspection Branch, Nepean, Ontario, Canada, February 23, 1995. Unpublished.

Aschbacher, P.W. and Feil, F.J. 1983. J. Agric. Food Chem. 31, 1150.

Ball, J.O. 1987. Magnitude of the residue, Terraclor and its metabolites in processed potatoes. MRID#40457401. Project No. UR-1407. Uniroyal Chemical Company, Inc., (Volume 30). Unpublished.

Ball, J.O. 1988a. Stability of Terraclor and allied metabolites in frozen wheat, corn, soybean, kidney beans, peppers, tomatoes, catsup, and dry tomato pomace. Project No. UR-1405. Uniroyal Chemical Company, Inc., (Volume 41). Unpublished.

Ball, J.O. 1988b. Magnitude of the residue, Terraclor and its metabolites in broccoli, MRID#40816702. Project No. UR-1408. Uniroyal Chemical Company, Inc., (Volume 40). Unpublished.

Ball, J.O. 1988c. Magnitude of the residue, Terraclor and its metabolites in cabbage, MRID#40816703. Project No. UR-1413. Uniroyal Chemical Company, Inc., (Volume 18). Unpublished.

Ball, J.O. 1988d. Magnitude of the residue, Terraclor and its metabolites in peppers, clewiston, Florida. MRID#40816705. Project No. UR-1410. Uniroyal Chemical Company, Inc., (Volume 28). Unpublished.

Ball, J.O. 1988e. Magnitude of the residue: Terraclor and its metabolites in beans. MRID#40816704. Project No. UR-1409. Uniroyal Chemical Company, Inc., (Volume 14). Unpublished.

Ball, J.O. 1988f. Magnitude of the residue, Terraclor and its metabolites in potatoes. MRID#40816701. Project No. UR-1414. Uniroyal Chemical Company, Inc., (Volume 29). Unpublished.

Ball, J.O. 1989a. Magnitude of the residue, Terraclor and its metabolites in peppers, clewiston, Florida. MRID#41521304. Project No. UR-1410 Addendum. Uniroyal Chemical Company, Inc., (Volume 27). Unpublished.

Ball, J.O. 1989b. Residues of PCNB and its metabolites and impurities in peanuts treated with Terraclor 2EC and Terraclor 4F in irrigation equipment. Report No. 41002507. Uniroyal Chemical Company, Inc., (Volume 26). Unpublished.

Ball, J.O. 1989c. Magnitude of the residue in Terraclor treated cottonseed and cottonseed fractions. Project No. UR-1412 Addendum. Uniroyal Chemical Company, Inc., (Volume 20). Unpublished.

Ball, J.O. 1990a. Terraclor storage stability in crops (cabbage and potatoes). Project No. UR-1404. Uniroyal Chemical Company, Inc., (Volume 40). Unpublished.

Ball, J.O. 1990b. Storage stability of PCNB and allied metabolites in frozen beans, peppers, tomatoes and tomato products. Project No. UR-1406. Uniroyal

Chemical Company, Inc., (Volume 42). Unpublished.

Ball, J.O. 1990c. Magnitude of the residue, Terraclor and its metabolites and impurities in tomatoes and processed tomatoes. MRID#41521301. Project No. UR-1411. Uniroyal Chemical Company, Inc., (Volume 31). Unpublished.

Ball, J.O. 1990d. Magnitude of the residue, Terraclor and its metabolites and impurities in tomatoes and processed tomatoes, at a two ppb quantitation limit. MRID#41521302. Project No. UR-1411 Addendum. Uniroyal Chemical Company, Inc., (Volume 32). Unpublished.

Ball, J.O. 1990e. Determination of Terraclor and its metabolites in beans and bean cannery waste, at a two ppb quantitition limit. MRID#41521303. Project No. UR-1409. Uniroyal Chemical Company, Inc., (Volume 16). Unpublished.

Ball, J.O. 1990f. Magnitude of the residue in Terraclor treated peanuts and peanut fractions. Report No. 41437601. Uniroyal Chemical Company, Inc., (Volume 25). Unpublished.

Batorewicz, W.B. 1988. Solubility of pentachlorobenzene in water. Project No. 88101. Uniroyal Chemical Company, Inc. (Volume 2). Unpublished.

Begum, S., Scheunert, J., Hague, A., Klein, W. and Karte, F. 1979. Pesticide Biochem. Physiol. 11, 189.

Cairns, F., Siegmund, E. and Masumoto, H. 1983. Bull. Environ. Contam. Toxicol. 31, 230.

Cairns, F., Siegmund, E. and Krick, F. 1987. J. Agric. Food Chem. 35, 433.

Daun, R.J. 1990. Pentachloronitrobenzene: nature of the residue in livestock - lactating goats. Report No. 6111-118. Huntingdon Analytical (Volume 4). Unpublished.

Gaydosh, K.A. 1990. Residue analytical methods - plant. Uniroyal Chemical Company, Inc., (Volume 11). Unpublished.

Gaydosh, K.A. 1991a. Storage stability of PCNB and its allied metabolite and impurities in cotton. Project No. RP-89066. Uniroyal Chemical Company, Inc., (Volume 43). Unpublished.

Gaydosh, K.A. 1991b. Storage stability of PCNB and its allied metabolite and impurities in peanuts. Project No. RP-89065. Uniroyal Chemical Company, Inc., (Volume 44). Unpublished.

Gaydosh, K.A. 1991c. PCNB and related metabolites and impurities in RTU-PCNB treated barley. MRID#41792601. Project No. UR-1418. Uniroyal Chemical Company, Inc., (Volume 33). Unpublished.

Gaydosh, K.A. 1991d. PCNB and related metabolites and impurities in RTU-PCNB treated field corn. MRID 41792605. Project No. UR-1416. Uniroyal Chemical Company, Inc., (Volume 34). Unpublished.

Gaydosh, K.A. 1991e. PCNB and related metabolites and impurities in RTU-PCNB treated peas. MRID#41792604. Project No. UR-1417. Uniroyal Chemical Company, Inc., (Volume 35). Unpublished.

Gaydosh, K.A. 1991f. PCNB and related metabolites and impurities in RTU-PCNB treated soybeans. MRID#41792602. Project No. UR-1416. Uniroyal Chemical Company, Inc., (Volume 36). Unpublished.

Gaydosh, K.A. 1991g. PCNB and related metabolites and impurities in RTU-PCNB treated sugarbeets. MRID#41792603. Project No. UR-1416. Uniroyal Chemical Company, Inc., (Volume 37). Unpublished.

Gaydosh, K.A. 1991h. PCNB and related metabolites and impurities in RTU-PCNB treated wheat. MRID#41792606. Project No. UR-1419. Uniroyal Chemical Company, Inc., (Volume 38). Unpublished.

Gaydosh, K.A. 1992. Magnitude of the residue: PCNB and related metabolites and impurities in cotton treated with Terraclor 2EC and Terraclor Flowable. MRID#42524115. Project No. RP-88001. Uniroyal Chemical Company, Inc., (Volume 21). Unpublished.

Gaydosh, K.A. 1993. Magnitude of the residue: Terraclor 75W, Terraclor 2EC, and Terraclor flowable on snap beans. #MRID43118202. Project No. RP-93009. Uniroyal Chemical Company, Inc., (Volume 15). Unpublished.

Gaydosh, K.A. 1994a. Magnitude of the residue: Terraclor 75W, Terraclor 2EC, and Terraclor flowable on dry beans. #MRID43118203. Project No. RP-93010. Uniroyal Chemical Company, Inc., (Volume 13). Unpublished.

Gaydosh, K.A. 1994b. Magnitude of the residue in Terraclor 10G and Terraclor 2E on cotton. Project No. RP-90034. Uniroyal Chemical Company, Inc., (Volume 19). Unpublished.

Gaydosh, K.A. 1994c. Magnitude of the residue in Terraclor 75W on peanuts. Project No. RP-90032. Uniroyal Chemical Company, Inc., (Volume 22) Unpublished.

Gaydosh, K.A. 1994d. Magnitude of the residue in Terraclor 10G and Terraclor 75W on peanuts. Project No. RP-90033. Uniroyal Chemical Company, Inc., (Volume 23). Unpublished.

Gaydosh, K.A. 1994e. Magnitude of the residue in Terraclor Flowable and Terraclor 2E on peanuts. Project No. RP-91022. Uniroyal Chemical Company, Inc., (Volume 24). Unpublished.

Gaydosh, K.A. 1995a. Quintozene - supporting technical information and data, prepared by Uniroyal Chemical Company, Inc., Bethany, Connecticut, USA, February 27, 1995. Unpublished.

Griffith, W.P. 1973. Determination of Terrazole (5-ethoxy-3-trichloromethyl-1,2,4-thiadiazole) and Terraclor (pentachloronitrobenzene) and allied metabolites in plant tissues or harvest samples. Report No. 84116. Uniroyal Chemical Company, Inc., (Volume 11). Unpublished.

Griffith, W.P. and Kuchar, E.J., (1975). Analytival investigations concerned with feeding Terraclor to chickens. Olin Corp. Report No. P 84132 (Volume 39). Unpublished.

Griffith, W.P., Kuchar, E.J. and Thomas, R.J., (1969). Analytival investigations concerned with Terraclor-Terrazole cow feeding studies. Olin Corp. Report No. P 84115 (Volume 39). Unpublished.

Lamoureux, G. and Rusness, D. 1980. J. Agric. Food Chem. 28, 1057.

Lamoureux, G., Gouot, J., David, D. and Rusness, D. 1981. J. Agric. Food Chem. 29, 996.

McManus, J.P. 1989. Metabolism of Pentachloronitrobenzene in the goat - metabolite identification. Report No. 8761. Uniroyal Cmemical Company, Inc. (Volume 4). Unpublished.

McManus, J.P. 1990a. Metabolism of Pentachloronitrobenzene in the goat - identification of metabolites in muscle. Report No. 8761-A Amendment I. Uniroyal Cmemical Company, Inc. (Volume 4). Unpublished.

McManus, J.P. 1990b. Metabolism of ^{14}C-Pentachloronitrobenzene (PCNB) in peanut. Report No. 8758. Uniroyal Chemical Company, Inc. (Volume 5). Unpublished.

McManus J.P. and Maisonet, F.A. 1990. Metabolism of pentachloronitrobenzene in cabbage-metabolite identification. Report No. 8756. Uniroyal Chemical Company, Inc. (Volume 5). Unpublished.

Murty, V. 1993. PCNB in confined rotational crops. Report No. MRID#41562905. Uniroyal Chemical Company, Inc. (Volume 7). Unpublished.

O'Grodnick, J.S. 1978a. Absorption and elimination characteristics of ^{14}C-labelled pentachloronitrobenzene in rats - pilot study. Report No. 77037. Olin Corp. (Volume 3). Unpublished.

O'Grodnick, J.S. 1978b. Characterization and identification of ^{14}C-PCNB Metabolites in rat urine and feces. Report No. 77037-2. Olin Corp. (Volume 3). Unpublished.

O'Grodnick, J.S. 1979. Identification of the polar metabolites of ^{14}C-PCNB after oral administration in rats. Report No. 78054. Olin Corp. (Volume 3). Unpublished.

Parkins, M.D. 1990a. Pentachloronitrobenzene: Nature of the residue in poultry-laying hens. Report No. 8762. Uniroyal Chemical Company, Inc. (Volume 4). Unpublished.

Parkins, M.D. 1990b. Appendix I - Pentachloronitrobenzene: Nature of the residue in livestock - laying hens (the in-life part). Report No. 6111-119. Hundingdon Laboratories. (Volume 4). Unpublished.

Parkins, M.D. 1990c. The metabolism of PCNB in field grown potatoes. Report No. 8758. Uniroyal Chemical Company, Inc. (Volume 5). Unpublished.

Parkins, M.D. 1991. Amendment I, Identification of bound residues. Report No. 8762 Amendment I. Uniroyal Chemical Company, Inc. (Volume 4). Unpublished.

Polakoff, B.M. 1987. Octanol/water partition coefficient of Terraclor. Project No. 8789. Uniroyal Chemical Company, Inc. (Volume 2). Unpublished.

Renner, G. and Klopfer, C. 1983. Chemosphere, 12, 967.

Selman, F. 1988. Determining the uptake and translocation of ^{14}C-PCNB used in the seed treatment of corn, wheat, soybeans, peas, and sugarbeets. Report No. 35972. ABC Laboratories (Volume 6). Unpublished.

Thomson, P.A. 1989. Determination of vapour pressure for PCNB using gas saturation. Project No. GRL-FR-10027. Uniroyal Chemical Company, Inc. (Volume 2). Unpublished.

TRIADIMEFON (133)

EXPLANATION

Triadimefon was first evaluated in 1979 and has been reviewed 10 times since. Initially the CXLs were based on combined residues of triadimefon and triadimenol, triadimenol being the principal metabolite and a pesticide in its own right. Separate limits were later established for triadimenol to accommodate its direct use.

After the 1989 JMPR had recommended separate limits, the 1992 Meeting re-examined earlier data on triadimefon and triadimenol as well as new information. The data were limited and the review was dependent to a large extent on observed trends in the ratio of triadimefon to triadimenol in trials in which both compounds had been measured separately following applications of triadimefon.

At the 1995 CCPR one delegation reported additional residue data to support its view that the 1:1 ratio of triadimefon to triadimenol used by the 1992 JMPR in estimating a maximum residue level for pineapple was unrealistic. These data are the focus of attention at the present Meeting. Other information on GAP and data on residues which were submitted to the Meeting will be held on file for a future JMPR.

METHODS OF RESIDUE ANALYSIS

The analytical method used for the analysis of triadimefon and triadimenol (and their hydroxylated metabolites KWG 1323 and KWG 1342 respectively) was supplied to the Meeting (Obrist *et. al.*, 1982). A validated modification of this method was used for the analysis of pineapples in the reported trials (Burger, 1992). The basic method involves extraction by refluxing with methanol/water, concentration, and incubation with cellulase enzyme to release conjugated metabolites. The extract is then partitioned into methylene chloride, cleaned up by GPC, and separated into two fractions on a preparative HPLC column. The first contains triadimefon and triadimenol and the second KWG 1342 and KWG 1323.

Triadimefon and triadimenol residues are quantified by GLC with an NPD. KWG 1342 and KWG 1323 are derivatized with trifluoroacetic anhydride before determination. Recoveries from peel and pulp fortified at 0.01, 0.02 and 0.05 mg/kg with triadimefon, triadimenol, KWG 1342 and KWG 1323 were 80-100% for triadimefon, 80-105% for triadimenol and ≥ 62% for the other two metabolites with significantly more variability. Similar results were obtained at higher fortification levels. The limit of determination for pulp and peel was reported to be 0.01 mg/kg, the lowest level validated.

All peel and pulp control values were <0.01 mg/kg in the validations, but not in the field trials, where the apparent residues of triadimefon were 0.003-0.006 mg/kg in the pulp and 0.003-0.01 mg/kg in the peel, and those of triadimenol <0.01-0.004 mg/kg in the pulp and all <0.01 mg/kg in the peel. If the highest control values in the peel and pulp are assumed, the apparent triadimefon residues in the untreated whole fruit would be approximately 0.0024 mg/kg assuming 80% pulp and 20% peel. This, with the acceptable recoveries from 0.01 mg/kg added to peel and pulp, gives support for a limit of determination of 0.01 mg/kg for whole fruit.

Stability of pesticide residues in stored analytical samples

Pineapple samples from the field trials were shipped and stored deep frozen for periods of less than 9 months from treatment. No studies of the storage stability of analytical samples of pineapple containing triadimefon or triadimenol residues were provided to the Meeting, although summarized data were supplied from storage stability studies of triadimefon in grapes and of both compounds in tomatoes,

wheat grain and wheat forage.

Triadimefon was reported to show ≤ 7% loss in each of the commodities tested after 552 days of freezer storage. Triadimenol showed ≤4% loss after 552 days from tomato, wheat grain and wheat forage. The loss from grapes was reported to be 15% after 118 days with an unexplained 0% after 238 or 552 days. Residues in potatoes decreased by 12 and 4% after 113 and 234 days respectively.

USE PATTERN

Information on current uses of triadimefon on pineapples in five countries was provided and is summarized in Table 1. It confirms the information provided to the 1992 JMPR for the USA and Zaire.

Table 1. Approved uses of triadimefon on pineapples.

Country	Application			PHI, days	Notes
	Formu-lation	No.	g ai/ha (g ai/hl)		
Brazil	WP	--	(7.5)	-	1 min. plant dip
Mexico	WP	1-2	125	50	field spray
Philippines	WP	1	25-50	-	field use
USA	WG or WP	1	(50)	-	Post-harvest, 3 min. dip
Zaire	EC	1	(10)	0	field use

RESIDUES RESULTING FROM SUPERVISED TRIALS

Pineapples. The current CXL of 3 mg/kg for the combined residues of triadimefon and triadimenol was based on the 1986 JMPR review showing total residues up to 2.2 mg/kg. Two other post-harvest trials in which the two compounds were determined separately indicated residues of triadimefon and triadimenol of 0.25 and 0.33 mg/kg (1979 JMPR) and 0.25 and 0.2 mg/kg (1983 JMPR). It was on the basis of these approximately 1:1 ratios and the observation that residues of triadimenol from dip uses are generally equal to or less than those of triadimefon that the 1992 JMPR estimated separate maximum residue levels of 1 mg/kg each for triadimefon and triadimenol. Another trial had indicated a 2.5:1 ratio, but this was from ten times the GAP application rate. The 1992 Meeting recognized the limitations of the data and concluded that additional trials were desirable.

The Meeting reviewed substantial new residue data (Burger, 1992) and relevant information on GAP. Two separate trials were conducted, both with three-minute dips (30 sec. in two cases) at a rate of 50 g ai/hl. In each case pineapples were treated separately on five successive days to allow for variability. Although the concentration was the same in both trials the volume of dip was 1 gallon in one trial and 7 gallons in the other. Samples were handled and stored under frozen conditions until analysis no more than 9 months after treatment. The results are shown in Table 2.

Table 2. Triadimefon and triadimenol residues in pineapples after post-harvest dip treatments with a 50% Dry Flowable formulation at 50 g ai/hl (Burger, 1992).

Day	Sample	% of Total Weight	Residues, mg/kg[1]			Ratio triadimefon/triadimenol
			Triadimefon	Triadimenol [2]	Total	
Experiment 1 (Miles 458-BL005, 1 gall dip)						
1	Pulp Peel Whole[3]	77 23 100	0.06 4.46 1.07	0.01 0.30 0.08	0.07 4.76 1.2	6 14.9 13.4
2	Pulp Peel Whole	74 26 100	0.1 5.58 1.52	<0.01 0.31 0.09	0.10 5.89 1.6	>10 18 16.9
3	Pulp Peel Whole	78 22 100	0.13 5.50 1.31	<0.01 0.40 0.1	0.13 5.91 1.4	>13 13.9 13.6
4	Pulp Peel Whole	77 23 100	0.14 7.03 1.73	<0.01 0.24 0.06	0.14 7.27 1.8	14 29.3 28.8
5	Pulp Peel Whole	78 22 100	0.15 6.28 1.5	<0.01 0.24 0.06	0.15 6.52 1.6	15 26.2 25
Experiment 2 (Miles 458-BL006, 7 galls dip)						
1[4]	Pulp Peel Whole	91 9 100	0.10 7.59 0.77	<0.01 0.49 0.05	0.10 8.08 0.82	>10 15.5 15.4
2[4]	Pulp Peel Whole	88 12 100	0.12 6.83 0.93	<0.01 0.36 0.05	0.12 7.19 0.98	>12 119 18.6
3	Pulp Peel Whole	88 12 100	0.07 6.26 0.81	<0.01 0.35 0.05	0.07 6.61 0.86	>7 17.9 16.2
4	Pulp Peel Whole	76 24 100	0.09 5.45 1.38	<0.01 0.37 0.1	0.09 5.82 1.50	>9 14.7 14.4
5	Pulp Peel Whole	83 17 100	0.06 5.56 1.0	<0.01 0.34 0.07	0.06 5.90 1.1	>6 16.3 14.3

[1] Samples were also analyzed for metabolites KWG 1342 and KWG 1323: no residues (<0.01 mg/kg) were found.
[2] <0.01 mg/kg treated as 0.01 mg/kg for calculation. [3] Calculated from weights of peel and pulp after removal of crown.
[4] 30 sec. dip.

APPRAISAL

Triadimefon has been reviewed many times since the first evaluation in 1979. MRLs were recommended for combined residues of triadimefon and triadimenol until 1989. Triadimenol being the principal metabolite of triadimefon and a pesticide in its own right. Triadimenol was evaluated for the first time in 1989, when a number of maximum residue levels were estimated to accommodate its direct use. On the basis of somewhat limited data the 1992 JMPR recommended separate MRLs for triadimefon and triadimenol. That Meeting considered additional data desirable.

triadimefon

The present Meeting reviewed comprehensive new data on the post-harvest use of triadimefon on pineapples to address a concern expressed at the 1994 CCPR (ALINORM 95/24, para 244) that the separate maximum residue levels of 1 mg/kg estimated for triadimefon and triadimenol were not supported by recent data. Other residue data and information on GAP submitted to the 1995 JMPR will be held on file in the FAO for evaluation by a future Meeting.

The Meeting confirmed that the limited data available to the 1992 JMPR were consistent with a ratio of triadimefon to triadimenol in the residue of 1:1 (or at most 2.5:1 from excessive applications). However, more recent results from 10 supervised post-harvest trials according to GAP support the views expressed at the CCPR that the ratio should be higher. The new data indicated that the triadimefon:triadimenol ratio from post-harvest dips according to GAP with a dry flowable formulation is 18 ± 5:1 under the conditions of the experiments in which samples were taken for analysis immediately after treatment.

The average residues of triadimefon in the whole fruit (calculated from separate analyses of peel and pulp) were 12.5 times those in the pulp and triadimenol residues were over 7 times those in the pulp, although the latter estimate is not exact since only one residue in pulp was measurable (0.01 mg/kg). The calculated residues in the whole fruit (peel + pulp, crown removed) of triadimefon ranged from 0.8 to 1.7 mg/kg (mean, 1.2 S.D. ± 0.33) and those of triadimenol from 0.05 to 0.1 mg/kg (mean 0.07 ± 0.02). The Meeting gave greater weight to the new data which show that shortly after dipping triadimefon residues are likely to exceed 1 mg/kg, and recommended that the current 1 mg/kg proposal be increased to 2 mg/kg.

The situation with triadimenol is less clear. The recent data clearly show that the triadimefon:triadimenol ratio shortly after treatment is much higher than in the 3 studies reviewed previously, which indicated a ratio of 1:1 or at the most 2.5:1. The recent data alone would support a maximum residue level of triadimenol of 0.1 mg/kg or perhaps 0.2 mg/kg, since most of the residues are close to 0.1 mg/kg. A level of 0.2 mg/kg might also be supported in view of the variability shown in the 10 trials (the ratio of triadimefon to triadimenol varied from 13.6:1 to 29:1).

However, because samples were taken immediately after treatment, the Meeting was concerned that the results did not reflect the maximum triadimenol residues likely to occur in commercial practice after storage. The Meeting therefore concluded that the new trials did not provide an adequate basis for revising the MRL of 1 mg/kg recommended by the 1992 JMPR for triadimenol and confirmed that recommendation.

Because it seemed that triadimenol residues could increase during commercial storage after treatment, the Meeting considered that information on triadimefon and triadimenol residues in commerce or at consumption was desirable for further confirmation of the estimates.

The analytical method used for triadimefon included enzymatic incubation to allow the determination of conjugated residues. Determination was by GLC with NP detection and the limit of determination was approximately 0.01 mg/kg in whole pineapples.

Only summary data from studies of the storage stability of analytical samples were provided with the report of the pineapple trials. These were not with pineapples, but with triadimefon or triadimenol on grapes, wheat grain and forage, tomatoes and potatoes. Generally the results would give credence to the pineapple trials if confirmed by the original reports. The Meeting concluded that any future periodic review of triadimefon and triadimenol would require submission of the full reports of storage stability studies, not only summary data.

RECOMMENDATIONS

The Meeting estimated the maximum residue level for pineapple shown below, which is recommended for use as an MRL.

Definition of the residue: triadimefon

Commodity		Recommendation (mg/kg)	
CCN	Name	Name	Current
FI 0353	Pineapple	2 Po	1 Po

FURTHER WORK OR INFORMATION

Desirable

Information on residues of triadimefon and triadimenol in pineapples in commerce or at consumption.

REFERENCES

Burger, R., 1992. Triadimefon (50DF) - Magnitude of the Residue on Pineapple. Data Requirements. EPA Guideline Ref. No: 171-4(d) Magnitude of the Residue Post harvest Treatments. Unpublished Miles Report No. 102649, May 15, 1992, submitted by Bayer AG.

Obrist, J., Leimkuehler, W. and Coffman, M., 1982. Phase 3 reformat of MRID 00149163: Residue Analysis Procedure for Bayleton and Metabolites in Barley and Wheat: Project Report No. 80488. Unpublished report, Mobay Corporation, original study data January 20, 1982.

TRIADIMENOL (168)

EXPLANATION

Triadimenol is a metabolite of triadimefon and was initially included in the definition of its maximum residue levels. The 1989 Meeting defined separate MRLs for triadimenol for the first time. The 1992 Meeting recommended the use of separate limits for triadimefon and triadimenol and a limit for pineapples of 1 mg/kg of triadimenol, based on triadimefon uses.

At the 1995 CCPR attention was drawn to the substantial recent results which demonstrated that on pineapples separate 1 mg/kg limits for triadimefon and triadimenol were inappropriate. The Meeting reviewed these and earlier results and its recommendations are given in the paper on triadimefon in this monograph.

APPRAISAL

At the 1994 CCPR attention was drawn to the availability of recent data on the use of triadimefon as a post-harvest dip, which were reported to show that the maximum residue levels of 1 mg/kg estimated by the 1992 JMPR for triadimefon and triadimenol resulting from the use of triadimefon on pineapples were inappropriate. The Meeting evaluated these data with other previously reviewed information and confirmed the previous estimate of 1 mg/kg for triadimenol.

A complete appraisal of the available data on triadimefon and triadimenol residues in pineapples is given above in the report on triadimefon (4.33).

FURTHER WORK OR INFORMATION

Desirable

Information on residues of triadimefon and triadimenol in pineapples in commerce or at consumption.

CORRECTIONS TO REPORT OF 1995 JMPR

Attention is drawn to two errors in the report of the 1995 Meeting.

(1). FENTHION, p. 121, para 6.

Change

The Meeting concluded that the data supported an increase in the maximum residue level and estimated a maximum level of 1 mg/kg to replace the previous estimate of 0.05 mg/kg.

to

Although the use pattern and data suggested a maximum residue level of 1 mg/kg, the Meeting could not suppsort this value on the basis of the risk assessment conducted.

The Meeting, therefore, recommended withdrawal of the existing CXL for milks (0.05mg/kg, FV).

The incorrect version was from a superseded draft. The recommendation to withdraw the CXL is correctly recorded in Annex I of both the Report and Evaluations.

(2). FENARIMOL, AnnexI, p. 213.

Change the recommended MRL for DF 0269 Dried grapes from 0.1 To **0.2 T** mg/kg.

The figure is correctly recorded in the text of the Report (p. 76) and in Annex I to these Evaluations.

ANNEX I

ACCEPTABLE DAILY INTAKES AND RESIDUE LIMITS PROPOSED AT THE 1995 MEETING

The Table of recommendations includes maximum Acceptable Daily Intakes (ADIs) and Maximum Residue Limits (MRLs). It should be noted that 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.

In general, the recommended MRLs listed for compounds which have been reviewed previously are additional to, or amend, those recorded in the reports of earlier Meetings. For compounds re-evaluated in the CCPR periodic review programme however, both new and previous recommendations are listed because such re-evaluations are regarded as replacing the original evaluation rather than supplementing it.

Limits recommended at meetings from 1965 to 1977 inclusive are summarized in document FAO/WHO 1978c.

Some ADIs are 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 following qualifications and abbreviations are used.

* 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
E	Extraneous Residue Limit (ERL).
F following recommendations for milk	The residue is fat-soluble and MRLs for milk and milk products are derived as explained in the introduction to Part 2 of the Guide to Codex Maximum Limits for Pesticide Residues and to Volume II of the Codex Alimentarius.
(fat) following recommendations for meat	The recommendation applies to the fat of the meat.
Po	The recommendation accommodates post-harvest treatment of the commodity.

PoP following recommendations for processed foods (classes D and E in the Codex Classification)	The recommendation accommodates post-harvest treatment of the primary food commodity.
T following ADIs	The ADI is temporary, and due for re-evaluation in the year indicated.
T following MRLs	The MRL is temporary, irrespective of the status of the ADI, until required information has been provided and evaluated.
V following recommendations for commodities of animal origin	The recommendation accommodates veterinary uses.
W in place of an MRL	The previous recommendation is withdrawn.

If a recommended MRL is an amendment, the previous value is also recorded. The absence of a figure in the "Previous" column indicates that the recommendation is the first for the commodity or group concerned.

The Table includes the Codex Classification Numbers (CCNs) of both the compounds and the commodities listed, to facilitate reference to the Guide to Codex Maximum Limits for Pesticide Residues and other Codex documents.

Commodities are listed in alphabetical order. This is a change from earlier practice where commodities were listed in the order of the "Types" in the Codex Classification of Foods and Animal Feeds, and in alphabetical order within each Type.

The change has been made to facilitate checking and comparison with the CCPR Tables of MRLs, which are in alphabetical order.

ACCEPTABLE DAILY INTAKES (ADIs) AND MAXIMUM RESIDUE LIMITS (MRLs)

Pesticide (Codex ref. No.)	ADI (mg/kg bw)	Commodity		Recommended MRL or ERL (mg/kg)	
		CCN	Name	New	Previous
Abamectin	0.001[1] 0.0002[2]	Notes: [1] for abamectin [2] for mixture of abamectin and ~-8,9 isomer			
Azinphos-methyl	0.005	TN 0660	Almonds	0.05	0.3
(002)		AM 0660	Almond hulls	5	-
		GC 0654	Wheat	W	0.2
		Residue: azinphos-methyl			
Benomyl** (069)	0.1	Notes: previous ADI 0.02 mg/kg bw. Residues in food should be compared with the ADI for carbendazim. Periodic review was for toxicology only.			
Bentazone (172)	0.1	Residue: Plant materials: sum of bentazone, 6-hydroxybentazone and 8-hydroxybentazone, expressed as bentazone. Animal materials: bentazone Notes: Note changed definition of residue for animal products, formerly "sum of bentazone and 2-amino-*N*-isopropylbenzamide, expressed as bentazone.			
Buprofezin	0.01	VC 0424	Cucumber	1	0.3 T
(173)		FC 0004	Oranges, Sweet, Sour	W	0.3 T
		VO 0448	Tomato	1	0.5 T
		Residue: buprofezin			
Captan (007)	0.1	Note: previous ADI maintained			
Carbendazim** (072)	0.03	Notes: previous ADI 0.01 mg/kg bw Residues in food should be compared against the ADI for carbendazim Periodic review was for toxicology only			
Cartap**	No ADI	VB 0041	Cabbages, Head	W	0.2
(097)		TN 0664	Chestnuts	W	0.1
		VL 0467	Chinese cabbage, type "Pe-tsai"	W	2
		HS 0784	Ginger, root	W	0.1
		FB 0269	Grapes	W	1
		DH 1100	Hops, dry	W	5
		FT 0307	Persimmon, Japanese	W	1
		VR 0589	Potato	W	0.1
		VR 0494	Radish	W	1
		CM 0649	Rice, husked	W	0.1
		VO 0447	Sweet corn (corn-on-the-cob)	W	0.1
		DT 1114	Tea, Green, Black (black, fermented and dried)	W	20
		Notes: previous ADI withdrawn. All previous recommendations for MRLs withdrawn. Not recorded as GLs.			
Chlorpyrifos	0.01	FC 0001	Citrus fruits	2	0.3
(017)		Residue: chlorpyrifos (fat-soluble)			
Dithianon	0.01	FS 0013	Cherries	5	1
(180)		Residue: dithianon			
Dithiocarbamates		AM 0660	Almond hulls	20 mb[1,2]	-
(105)		TN 0660	Almonds	0.1*[2] mz, mb	-
		VS 0621	Asparagus	0.1[2] mz	-
		FI 0327	Banana	2[2] mz	1
		GC 0640	Barley	1[2] mz	-

Pesticide (Codex ref. No.)	ADI (mg/kg bw)	Commodity		Recommended MRL or ERL (mg/kg)	
		CCN	Name	New	Previous
		AS 0640	Barley straw and fodder, dry	25[2] mz, mb	-
		VB 0041	Cabbages, Head	5[2] mz, mb	-
		VR 0577	Carrot	1[2] mz	0.5
		VS 0624	Celery	W[2]	5
		FS 0013	Cherries	W[2]	1
		VP 0526	Common bean (pods and/or immature seeds)	1[3] mt	W[2]
		VL 0510	Cos lettuce	10[2] mb	-
		FB 0265	Cranberry	5[2] mz	-
		VC 0424	Cucumber	2[2] mz, mb	0.5
		FB 0021	Currants, Black, Red, White	10 mz mt	10[2]
		MO 0105	Edible offal (mammalian)	0.1 mz mt	0.1[2]
		PE 0112	Eggs	0.05*[2] mz	-
		VL 0476	Endive	W[4]	1
		VA 0381	Garlic	0.5[2] mz	-
		FB 0269	Grapes	5 mz mt, mb, pb	5
		DH 1100	Hops, dry	30[3] mt	-
		VL 0480	Kale	15[2] mz, mb	-
		VA 0384	Leek	0.5[2] mz	-
		VL 0482	Lettuce, Head	10 mz, mb, mt	10[2]
		AS 0645	Maize fodder	2[2] mz	-
		FC 0003	Mandarins	10[2] mz	-
		FI 0345	Mango	2[3] mz	-
		MM 0095	Meat	0.02* mz, mt	0.02*[2]
		VC 0046	Melons, except Watermelon	0.5[2] mz, pb	1
		ML 0106	Milks	0.05* mz, mt	0.05*[2]
		VA 0385	Onion, Bulb	0.5[2] mz, pb	-
		FC 0004	Oranges, Sweet, Sour	2[2] mz	-
		FI 0350	Papaya	5[2] mz	-
		FS 0247	Peach	W[5]	3
		SO 0697	Peanut	0.1*[2] mz	-
		AL 0697	Peanut fodder	5[2] mz	-
		VO 0445	Peppers, Sweet	1[2] mz, mb	-
		FS 0014	Plums (including Prunes)	W[2]	1
		FP 0009	Pome fruits	5 mz mt, pb	5[2]
		VR 0589	Potato	0.2 mz, mt, mb, pb	0.2[2]
		PM 0111	Poultry, Edible offal of	0.1[2] mz	-
		PO 0110	Poultry meat	0.1[2] mz	-
		VC 0429	Pumpkins	0.2[2] mz	-
		VA 0389	Spring onion	10[2] mb	-
		VC 0431	Squash, Summer	1[2] mz	-
		FB 0275	Strawberry	W[5]	3
		VR 0596	Sugar beet	0.5[2] mz, mb	-
		AV 0596	Sugar beet leaves or tops	20[2] mz, mb	-
		VO 0447	Sweet corn (corn-on-the-cob)	0.1*[2] mz	-
		VO 0448	Tomato	5 mz mt, mb, pb	5[2]
		VC 0432	Watermelon	1[2] mz, mb	-

Pesticide (Codex ref. No.)	ADI (mg/kg bw)	Commodity		Recommended MRL or ERL (mg/kg)	
		CCN	Name	New	Previous
		GC 0654	Wheat	1 mz, mb, mt	1[2]
		AS 0654	Wheat straw and fodder, dry	25 mz, mb, mt	25[2]
		VC 0433	Winter squash	0.1[2] mz	-
		Residue: total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg. Notes: MRLs refer to total residues from the use of any or each of the groups of dithiocarbamates. Note revised wording of residue definition. [1] Based on trials with mb maneb, mt metiram, mz mancozeb, pb propineb. Underlined compounds are those on which estimates of maximum residue levels are mainly based. [2] 1993 recommendation. [3] 1995 recommendation. [4] 1995 recommendation, omitted in 1993 in error. [5] Withdrawal recommended by 1993 JMPR; withdrawn by 21st CAC.			
Ethephon (106)	0.05	Note: previous ADI maintained			
Fenarimol*	0.01	AB 0226	Apple pomace,dry	5 T	-
(192)		VS 0620	Artichoke, Globe	0.1 T	-
		FI 0327	Banana	0.2 T	-
		MO 1280	Cattle, kidney	0.02* T	
		MO 1281	Cattle, liver	0.05 T	
		MM 0812	Cattle meat	0.02* T	
		FS 0013	Cherries	1 T	-
		DF 0269	Dried grapes (= Currants, Raisins and Sultanas)	0.2 T	-
		FB 0269	Grapes	0.3 T	-
		VC 0046	Melons, except Watermelon	0.05 T	-
		FS 0247	Peach	0.5 T	-
		TN 0672	Pecan	0.02* T	-
		VO 0445	Peppers, Sweet	0.5 T	-
		FP 0009	Pome fruits	0.3 T	-
		FB 0275	Strawberry	1 T	-
		Residue: fenarimol			
Fenpropimorph*	0.003	GC 0640	Barley	0.5	-
(188)		AS 0640	Barley straw and fodder, dry	5	-
		AV 1051	Fodder beet leaves or tops	1	-
		GC 0647	Oats	0.5	-
		AS 0647	Oat straw and fodder, dry	5	-
		GC 0650	Rye	0.5	-
		AS 0650	Rye straw and fodder, dry	5	-
		VR 0596	Sugar beet	0.05*	-
		AV 0596	Sugar beet leaves or tops	1	-
		GC 0654	Wheat	0.5	-
		AS 0654	Wheat straw and fodder, dry	5	-
		Residue: fenpropimorph Note: First review of residue and analytical aspects. Toxicology was reviewed in 1993.			
Fenpyroximate* (193)	0.01	Note: The Meeting estimated a maximum residue level for apples, but owing to the lack of critical supporting data this is not recommended for use as an MRL.			

Pesticide (Codex ref. No.)	ADI (mg/kg bw)	Commodity		Recommended MRL or ERL (mg/kg)	
		CCN	Name	New	Previous
Fenthion**	0.007	FP 0226	Apple	W	2
(039)		FI 0327	Banana	W	1
		VB 0041	Cabbages, Head	W	1
		VB 0404	Cauliflower	W	1
		FS 0013	Cherries	2	2
		FC 0001	Citrus fruits	W	2
		JF 0001	Citrus juice	W	0.2
		VP 0526	Common bean (pods and/or immature seeds)	W	0.1
		FB 0269	Grapes	W	0.5
		VL 0482	Lettuce, Head	W	2
		FC 0003	Mandarins	0.5	2[1]
		MM 0095	Meat	W	2 (fat) V
		ML 0106	Milks	W	0.05 F V
		OC 0305	Olive oil, virgin	3	1
		FT 0305	Olives	1	1
		VA 0385	Onion, Bulb	W	0.1
		FC 0004	Oranges, Sweet, Sour	0.5	2[1]
		FS 0247	Peach	W	2
		FP 0230	Pear	W	2
		VP 0063	Peas (pods and succulent = immature seeds)	W	0.5
		FS 0014	Plums (including Prunes)	W	1
		VR 0589	Potato	W	0.05
		GC 0649	Rice	W	0.1
		CM 0649	Rice, husked	0.05	
		VC 0431	Squash, Summer	W	0.2
		FB 0275	Strawberry	W	2
		VR 0508	Sweet potato	W	0.1
		VO 0448	Tomato	W	0.5
		GC 0654	Wheat	W	0.1
		VC 0433	Winter squash	W	0.2
		Residue: sum of fenthion, its oxygen analogue and their sulfoxides and sulfones, expressed as fenthion (fat-soluble) Notes: previous ADI 0.001 mg/kg bw. [1]Group MRL			
Flusilazole (165)	0.001	Note: previous ADI maintained			
Folpet (041)	0.1	Note: previous temporary ADI 0.01 mg/kg bw			
Haloxyfop* (194)	0.0003	Note: the Meeting estimated a number of maximum residue levels, but owing to the lack of critical supporting data these are not recommended for use as MRLs.			
Iprodione (111)	0.06	Note: previous ADI 0.2 mg/kg bw			
Metalaxyl	0.03	FB 0275	Strawberry	W	0.2
(138)		Residue: metalaxyl			
Metiram* (186)		Residue: total dithiocarbamates, determined as CS_2 evolved during acid digestion and expressed as mg CS_2/kg. MRLs are listed under dithiocarbamates and refer to			

Pesticide (Codex ref. No.)	ADI (mg/kg bw)	Commodity		Recommended MRL or ERL (mg/kg)	
		CCN	Name	New	Previous
		total residues from the use of any or each of the groups of dithiocarbamates. Note: First review of residue and analytical aspects. Toxicology was reviewed in 1993.			
Parathion** (058)	0.004	Notes: previous ADI 0.005 mg/kg bw Acute RfD: 0.01 mg/kg bw Periodic review was for toxicology only			
Parathion-methyl** (059)	0.003	Notes: previous ADI 0.02 mg/kg bw Acute RfD: 0.03 mg/kg bw Periodic review was for toxicology only			
Penconazole (182)	0.03	DF 0269	Dried grapes (= Currants, Raisins and Sultanas)	0.5	-
		Residue: penconazole			
Piperonyl butoxide** (062)	0.2	Notes: previous ADI 0.03 mg/kg bw. Periodic review was for toxicology only.			
Profenofos	0.01	SO 0691	Cotton seed	2	3
(171)		MM 0095	Meat	0.05*	0.02*
		VO 0445	Peppers, Sweet	0.5	-
		DT 0171	Teas (Tea and Herb teas)	W	0.5
		Residue: profenofos			
Quintozene**	0.01	FI 0327	Banana[1]	W	1
(064)		VB 0400	Broccoli	W	0.02
		VB 0041	Cabbages, Head	W	0.02
		VD 0526	Common bean (dry)	W	0.2
		VP 0526	Common bean (pods and/or immature seeds)	W	0.01
		SO 0691	Cotton seed	W	0.03
		VL 0482	Lettuce, Head[1]	W	3
		SO 0697	Peanut	W	2
		SO 0703	Peanut, whole	W	5
		VO 0445	Peppers, Sweet	W	0.01
		VR 0589	Potato[1]	W	0.2
		VO 0448	Tomato	W	0.1
		Residue: for plant commodities: quintozene for animal commodities: sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene (fat-soluble) Notes: previous ADI 0-0.007 mg/kg bw The ADI is for quintozene containing less than 0.1% hexachlorobenzene The above definitions of the residue are for enforcement purposes. For risk assessment purposes both plant and animal commodities are defined as the sum of quintozene, pentachloroaniline and methyl pentachlorophenyl sulfide, expressed as quintozene (fat-soluble). The previous recommendations for MRLs are withdrawn in the absence of critical supporting studies needed for periodic review. [1] These recommendations are also withdrawn because uses have been discontinued and/or no residue data were available.			
Thiophanate-methyl** (077)	0.02	Notes: previous ADI 0.08 mg/kg bw. Periodic review was for toxicology only.			
Triadimefon	0.03	FI 0353	Pineapple	2 Po	1 Po
(133)		Residue: triadimefon			
Vinclozolin (159)	0.01	Note: previous ADI 0.07 mg/kg bw.			

Joint FAO/WHO Meeting on Pesticide Residues
Rome, 20-29 September 1999

The Annual Joint FAO/WHO Meeting on Pesticide Residues (JMPR) was held in Rome, Italy, from 20 to 29 September 1999. The following information is an extract of the results of this meeting with the aim of making them accessible to interested parties at an early date.

The Meeting evaluated 31 pesticides, including one new compound and 12 compounds undergone a complete re-evaluation within the Periodic Review Programme of the Codex Committee on Pesticide Residues (CCPR).

The Meeting allocated Acceptable Daily Intakes (ADIs) and Acute Reference Doses (Acute RfDs), estimated maximum residue levels which it recommended for use as Maximum Residue Limits (MRLs) by the CCPR, and estimated Supervised Trials Median Residue (STMR) level as a basis for the estimation of the dietary intakes of residues of the pesticides reviewed. The estimates are recorded in the Table below.

As in 1998, the Meeting devoted particular attention to the estimation of the dietary intakes of the pesticides reviewed in relation to their ADIs. Those compounds whose estimated dietary intakes might, on the basis of the available information, exceed their ADIs are marked with footnotes. For the first time , the Meeting also estimated the acute dietary risk of some of the pesticides.

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 Residue Limits for Pesticides (*Codex Alimentarius,* Vol.2B) and other documents and working documents of the Codex Alimentarius Commission.

The Table will be included as Annex 1 to the JMPR – Report 1999 to be published early in 2000. This report will provide full details of the reasons for the recommendations, of the calculations of dietary intake and of the assessment of dietary risk of the pesticides reviewed. As usual this table will also become the Annex to the "JMPR – Evaluations 1999 PartI – Residues" to be published later in 2000.

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, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
Bentazone (172)		Acute RfD: Unnecessary				
Bitertanol **	0.01	JF 0226	Apple juice			0.0336
(144)		AB 0226	Apple pomace, Dry			1.78
			Apple pomace, Wet			0.648
			Apple sauce			0.0346
		FS 0240	Apricot	W[1]	1	
		FI 0327	Banana	0.5	0.5	0.075
		GC0640	Barley	0.05 *		0
		AS 0640	Barley straw and fodder, Dry	0.05 *		0
		AL1030	Bean forage (green)	W[1]	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[1]	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	0.17
		AF 0647	Oat forage (green)	0.05 *[2]	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	0.17
		SO 0697	Peanut	W[1]	0.1 *	
		AL 1270	Peanut forage (green)	W[1]	20	
		FS 0014	Plums (including prunes)	2	2	0.34
			Plum jam			0.21

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		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 *[2]	0.1 *	0.05
		AS 0650	Rye straw and fodder, Dry	0.05 *	0.1 *	0
		VO0448	Tomato	3		0.76
		JF 0448	Tomato juice			0.1
			Tomato paste			1.6
			Tomato preserve			0.28
		GC0653	Triticale	0.05 *		0
			Triticale straw and fodder, Dry	0.05 *		0
		GC0654	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-hydroxy bitertanol and its acid hydrolyzable conjugates The residue is fat soluble [1] Previous recommendation should be withdrawn [2] Dry weight Acute RfD: Unnecessary Periodic review was for residues only				
Buprofezin (173)	0.01	FC 0004	Oranges, Sweet, Sour	0.5	W	0.011
			Orange juice			0.012
			Orange pulp, dry			0.27
		Residue (for MRLs and STMRs): buprofezin The residue is fat soluble				
Carbofuran (096)	0.002	FC 206	Mandarin	0.5		
		Residue (for MRLs and STMRs): sum of carbofuran and 3-hydroxy- carbofuran, expressed as carbofuran. Acute RfD: May be necessary but has not yet been established.				
Carbosulfan (145)	0.01	FC 206	Mandarin	0.1		
		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	W	0.81
		AL 0061	Bean fodder (hay)	10		1.8
		AL 1030	Bean forage (vines)	5		1.5
		MO 1280	Cattle, Kidneys	W	0.2*	
		MO 1281	Cattle, Liver	W	0.2*	

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		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*	
		MM 0095	Meat (from mammals other than marine mammals)	0.2*		0
		ML 0106	Milks	0.05*		0
		MO 0105	Edible offal (mammalian)	0.2*		0
		PE 0112	Eggs	0.05*		0
		OC 0697	Peanut oil, Crude			0.52
		OR 0697	Peanut oil, Edible			0.12
		VR 0589	Potato[1]	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	W	0.06
		OC 0702	Sunflower seed oil, Crude	0.1*	W	0.012
		JF 0448	Tomato juice			0.27
			Tomato paste			1.2
			Tomato puree			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 1 STMRs 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			0.0572
			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 fruit	0.3	2	0.04
		Residue (for MRLs and STMRs): Diazinon The residue is fat-soluble [1] Estimated dietary intake might, on the basis of the available information, exceed the ADI. [2] STMR proposed by the 1996 JMPR				
Dimethipin ** (151)	0.02	Acute RfD: 0.02 mg/kg bw Previous 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, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		Residue (for MRLs and STMRs): dinocap Acute RfD: 0.008 mg/kg bw				
Ethephon (106)	0.05	VC4199	Cantaloupe	1	1	0.24 [1]
		DF 0269	Dried grapes	5		0.84
		FB 0269	Grapes	1	1	0.31
		VO 0051	Peppers	5	30	0.98
		FI 0353	Pineapple	2	1	0.13
			Pineapples canned			0.036
			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] Cantaloupe: 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	1.86
		Residue (for MRLs and STMRs) ethoxyquin Acute RfD: Unnecesary 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	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	0.05	0.05*	0.01
		VR 0577	Carrot	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	0.1	0.1	0.02

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P 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	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	0.5		0.055
		FI 0353	Pineapple	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	0.5	0.2	0.05
		JF 0448	Tomato juice			0.05
		VC 0432	Watermelon	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.				
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: N-[3-(4-phenylisobutyric acid)-2-methyl propyl]- 2,6(cis)-dimethyl morpholine, expressed as fenpropimorph. Acute RfD: May be necessary but has not yet been established.				
Fenpyroximate (193)	0.01	FP 0226	Apples	0.3		0.09
		JF 0226	Apple juice			0.04
			Apple puree			0.05

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		MO 1280	Cattle kidney	0.01*		
		MO 1281	Cattle liver	0.0 *		
		ML 0812	Cattle milk	0.005* F		0.002
		MM 0812	Cattle meat	0.02 (fat)		0.01
		FB 0269	Grapes	1		0.07
		DH 1100	Hops	10		4.4
		FC 0004	Oranges, Sweet, Sour	0.2		0.01
			Beer			0.004
			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	W	3.1
		JF 0226	Apple juice			0.11
			Apple pomace, Wet			8.1
		VC 0424	Cucumber	1	W	0.36
		DF 0269	Dried grapes (currants, raisins and sultanas)	40	W	8.0
		FB 0269	Grapes	10	W	2.5
		JF 0269	Grape juice			0.0075
		VL 0482	Lettuce, Head	50		14
		VC 0046	Melons, except watermelon	3	W	0.41
		VA 0385	Onion, Bulb	1		0.07
		VR 0589	Potato	0.1	W	0.01
		FB 0275	Strawberry	5	W	1.6
		VO 0448	Tomato	3	W	0.90
			Tomato puree			0.025
			Tomato paste			0.025
			Wine			0
		Residue (for MRLs and STMRs): folpet 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
		Residue (for MRLs and STMRs): Sum of glufosinate-ammonium, 3-(hydroxy(methyl)phosphinoyl)propionic acid and N-acetyl-glufosinate calculated 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 value Previous ADI: 0.02 mg/kg bw (1991) Acute RfD: Unnecessary				

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
Malathion ** (049)	0.3	AL 1021	Alfalfa, Forage	500		157
		AL 1020	Alfalfa, fodder	200		17
		FP 0226	Apple	W	2	
		VS 0621	Asparagus	1		0.305
		VP 0071	Beans (dry)	2	8 Po	0.36
		BP 0061	Beans, except broad beans and soya beans	1		0.31
		FB 0264	Blackberries	W	8	2.6
		FB 0020	Blueberries	10	0.5	2.27
		VB 0400	Broccoli	W	5	
		VB 0041	Cabbages, Head	W	8	0
		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	1.35
		AL 1023	Clover	500		231
		AL 1031	Clover, Hay or fodder	150		33.5
		FC 0001	Citrus fruits	W	4	
		VP 0526	Common bean (pods and/or immature seeds)	W	2	0.31
		SO 0691	Cotton seed	20		4.7
		OC 0691	Cotton seed oil, Crude	13		3.15
		OR 0691	Cotton seed oil, edible	13		3.06
			Cotton seed, Meal	1.4		6.58
			Cotton seed oil, B&D			0.038
		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	0.86
		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		4.7
		AF 0645	Maize forage	10		0.2
		VL 0485	Mustard, Green	2		0.07
		AO51900	Nuts (whole in shell)	W	8	
		VA 0385	Onion, Bulb	1		0.23
		VA 0389	Spring onion	5		0.52
		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
		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	
		VL 0502	Spinach	3	8	0.35
		FB 0275	Strawberry	1	1	0.25
		VO 0447	Sweet corn	0.02		0.01

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		GC 0651	Sorghum	3		0.235
		VO 0448	Tomato	0.5	3	0.21
		VJ 0448	Tomato, Juice	0.01		0.00
			Tomato, Wet pomace			0.20
			Tomato, Dry pomace			1.6
			Tomato, Puree			0.07
			Tomato, Catsup			0.09
		VR 0506	Turnip, Garden	0.2	3	0.05
		VL 0506	Turnip, Greens	5		1.195
		GC 0654	Wheat, Grain	0.5		0.04
			Wheat, Forage	20		4.14
		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 *	
		SO 0495	Rape seed	W	0.05 *	
		VR 0596	Sugar beet	W	0.05 *	
		VO 0447	Sweet corn (corn-on-the-cob)	W	0.05 *	
		FB 0275	Strawberry	1		0.44
		Residue (for MRLs and STMRs): sum of methiocarb, methiocarb sulfoxide and methiocarb sulfone, expressed as methiocarb. Periodic review was for residues only.				

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
Permethrin ** (120)	0.05[1]	Acute RfD: Unnecessary [1]For technical-grade permethrin with cis:trans ratios of 25:75 to 40:60. Previous 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	FP 0009	Pome fruits	2	W[1]	0.8
		FS 0012	Stone fruits	2		0.45
		TN 0660	Almonds	0.1		0.05
		TN 0666	Hazelnuts	0.05*		0.05
		TN 0678	Walnuts	0.05*		0.05
			Apple compote			0.1
		Residue (for MRLs and STMRs): phosalone The residue is fat soluble [1]For apple Acute RfD: May be necessary but has not yet been established.				
Propargite ** (113)	0.01	Acute RfD: Unnecessary Previous ADI: 0.15 mg/kg bw Periodic review was for toxicology only.				
Propylene thiourea	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 Previous 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
			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

Pesticide	ADI, Mg/kg bw	Commodity		Recommended MRL, mg/kg		STMR, STMR-P mg/kg
(Codex reference no.)		CCN	Name	New	Previous	
		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	FP 0009	Pome fruit	1	1	0.17
			Apple pomace, Wet			0.425
			Apple juice			0.021
			Apple puree			0.0425
		FB 0269	Grapes	1	0.5	0.25
			Grape pomace, Wet			0.675
			Wine			0.0625
		Residue (for MRLs and STMRs): tebufenozide The residue is fat soluble.				