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Organic Matter Of Buried Soils: Evolution, Structure, Function

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Abstract

The study of soil organic matter (SOM) evolution in buried soils enables the cognition of the regularities of the largest carbon reservoir transformation, which plays a critical role in carbon sequestration and sustainable biosphere functioning.
We investigated SOM of buried soils in forest-steppe zone with dates of burial, not exceeding 2000 years on the territory of Belgorod region of Russia. Over 400 years of burial, content of SOM carbon steady at the level of 0.7%. Over the next 1600 years the SOM carbon content of organic compounds remains unchanged (0,66%). Reducing the amount of organic matter is accompanied by sharp changes in its qualitative composition. In the buried soils dramatically decreases the CO_2 emissions directly associated with the time of burial.
According to the spectra the 13C-NMR of the humic acids (HA) molecular structure evolution ends 400 years. 13C-NMR spectra of HA 400 - and 2000-year-old buried soils are almost identical. The change in molecular structure causes a natural decrease of functional parameters of HA significantly reduced their physiological activity, which is manifested in reduced productivity of photosynthesis in the experiment with the test culture of *Chlorella vulgaris*.

Key words: buried soils, humic acids evolution, 13C-NMR.

Introduction

The study of the evolution of humic substances (HS) in the context of deficient biological cycle is of great fundamental and applied importance. It gives the key to the knowledge of regularities of transformation this largest reservoir of carbon, playing the most important role in the sustainable functioning of the modern biosphere. In condition humus horizons of vergin soils it is difficult to give an accurate estimation of the parameters of biological cycle, and buried soils in this sense is a unique object. Humus horizon of these soils screened by bury layer from the active influence of the biological cycle and circulation of fresh organic residues.
In the scientific paleosols literature is found the view that the HS's composition and your extend can be easily reconstruct the biohydrothermodynamics conditions of formation of these soils. However, relatively few works devoted to the processes of evolution of HS in burial soils.

Methodology

We investigated buried soils of forest-steppe zone with dates of burial, not exceeding 2 thousand years. It can be assumed that climatic and biohydrothermodynamics conditions on the territory of Belgorod region for the period little changed, so the comparison of buried soils HS with HS modern virgin soils is quite correct. In our work, was studied in Dark-grey forest soils (Haplic Greyzems – FAO, Greyic Phaeozems Albic WRB) on site and in the vicinity of the site "Forest on the Vorskla" of nature reserve "Belogorie" of Belgorod region: virgin, buried since 1974, buried 1937 and buried nearly 2000 years ago (the soil under the mound of ancient hill fort of Scythian time). In addition, we examined the Chernozem (Haplic Chernozems) buried under a ground shaft of Belgorod defense line (1635-1658 years). In addition to the study of physic-chemical characteristics of soils from humus horizons of all studied soils us was isolated preparations of humic acids (HA). They had studied the elemental composition, the concentration of free radicals (ESR method) and molecular structure (method 13C-NMR).

Results and discussion

After burial in soil as a result of discontinuing the receipt of fresh organic residues into humus horizon after beyond the active root layer and lower soil-forming potential of their environment starts the active mineralization of SOM, the speed of which decreases with time. To the 400-year age of the SOM stabilized at the level of 0.7% (organic carbon). (Fig 1.) Over the next 1600 years the organic carbon content remains unchanged (0.66%). Reducing the SOM amount is accompanied by sharp changes in its qualitative composition. The ratio of HA/FA grows from 1.0 (virgin) 2.5–3.0 (buried), which indicates the destruction of fulvic acid (FA), as the less stable fraction of HS. In the buried horizons dramatically decreases the CO2 emissions directly associated with the time of burial, which indicating that the reduction of biological activity in these soils.

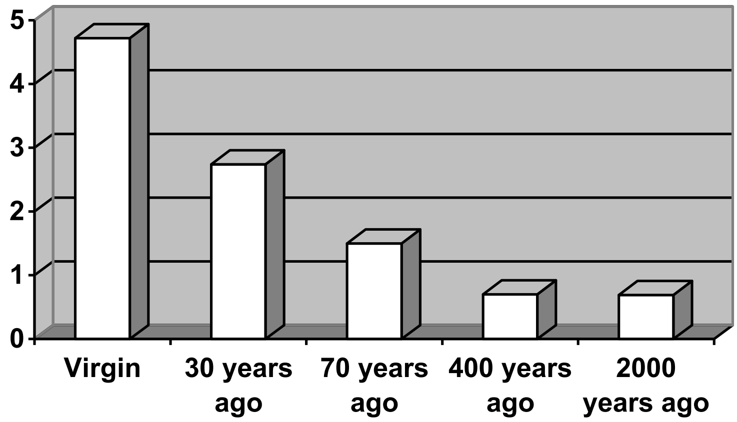

Fig 1. Content of SOM (C,%) in the buried soils.

If we compare the spectra of the 13C-NMR HA virgin and buried soils, it is possible to note the relative decrease in the number of aliphatic chains (area of 20 to 40 ppm in the spectrum of 13C-NMR), which is accompanied by increasing content of aromatic structures (area 106 – 170 ppm). This leads to an increase in aromaticity of HA molecules in the buried soils of almost five times.

But, according to the spectra the 13C-NMR evolution of the HA molecular structure is in the direction of the relative increase in the aromatic structures content, and at the expense of condensed polycoupling coal-like structures (Chukov, 1985; Schulten H.R., Schnitzer M. 1997; e.a.), giving a broad signal in the 129 ppm chemical shift.

This fact is explained by the higher resistance in aromatic rings compared to the aliphatic chains, which are much less resistant to the attacks of “hungry” soil microorganisms in conditions of sharp shortage of fresh organic residues.

It should be noted that the evolution of the molecular structure of HA ends 400 years. Spectra the 13C-NMR HA 400 - and 2000-year-old soils are almost identical (Fig. 2, 3). This suggests that over the 400 years old HS buried soils have evolved and it is in equilibrium with biohydrothermodynamics environmental conditions. In such a steady and equilibrium state, it stays all further years. In fact, such a structure of HA can be called "humic coal" is really close in composition to coal structures.

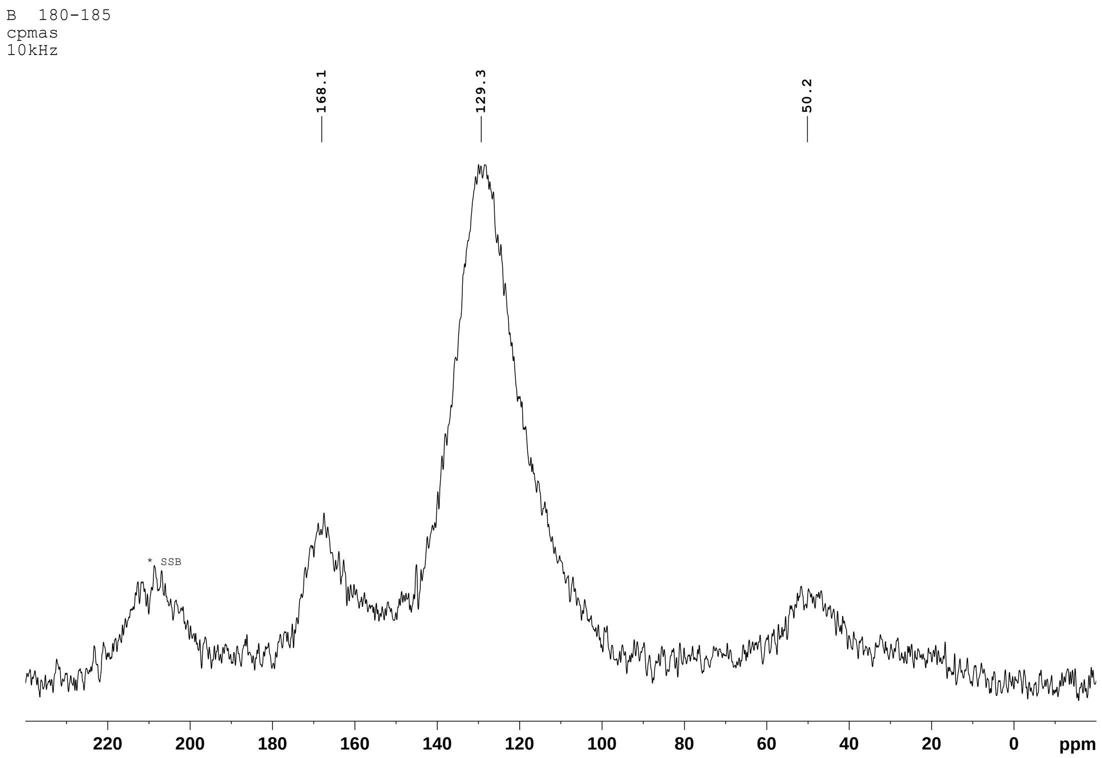

Fig. 2. 13C-NMR spectrum of HA buried soil 400 ears ago.

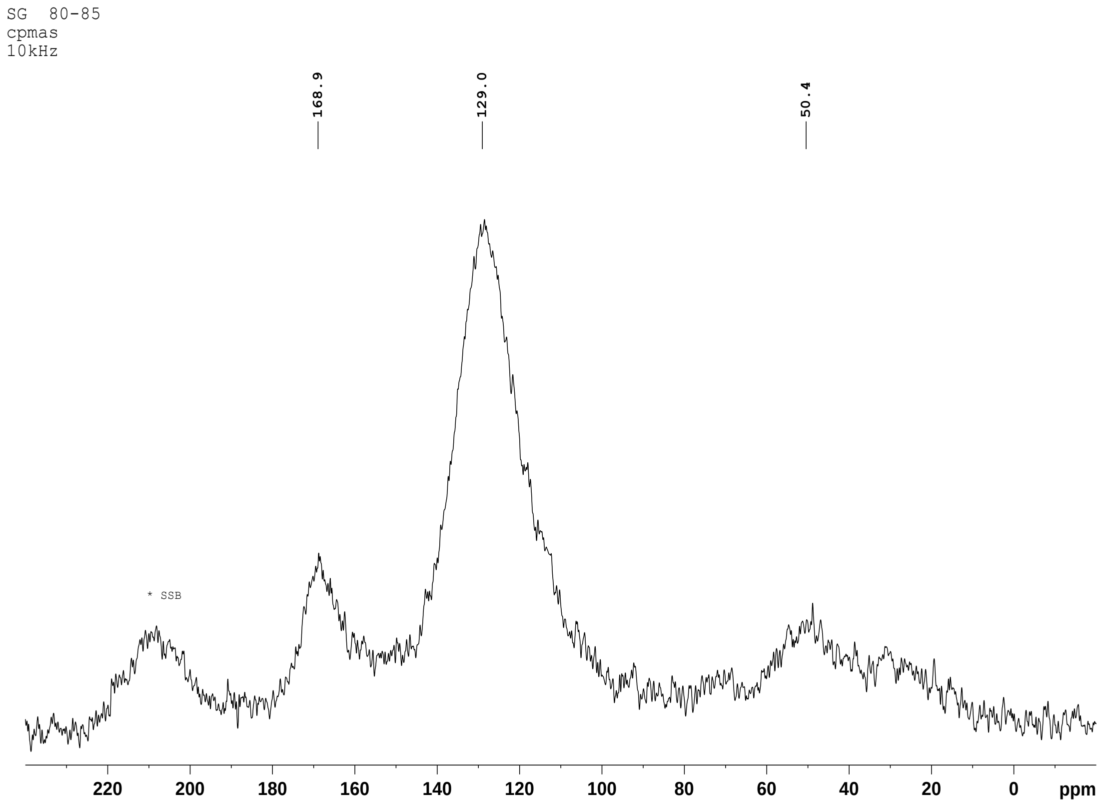

Fig. 3. 13C-NMR spectrum of HA buried soil 2000 ears ago.

The concentration of free radicals is of great importance for their biochemical activity and other functions. The data in the table 1 show how strongly influenced by burial this structural parameter HA. This fact is confirmed by the results of experience in the coleoptiles of *Maize*.

Table 1. The free radical concentration (FRC, spin/g) and physiological activity (PHA, conventional units) of HA of virgin, tillable arable and buried soil.

Soil	FRC, 10^{15} spin/g	PHA, c.u.
Haplic Chernozems		
virgin	355,1	0,80
tillable	114,2	0,42
buried	30,2	0,30
Haplic Greyzems		
virgin	107,8	0,56
tillable	93,9	0,35
buried	52,2	0,28
Sod-podzolics (Podzoluvisols)		
virgin	7,8	0,38
tillable	6,5	0,15
buried	9,1	-0,17

Of course, a significant evolution in quantitative and qualitative composition of the SOM and the associated strong structural changes of buried soils affect their functional properties, which we estimated on the most important (from the point of view of the participation of HA in soil fertility) to parameter of physiological activity.

Table 2. The correlation coefficients between *Chlorella vulgaris* total photosynthesis and the concentration of free radicals in preparations of HA.

HA, %	Correlation coefficient, p=0,05
0.001	0.95
0.003	0.84
0.004	0.75
0.005	0.83

We were able to trace a significant relationship to physiological activity of HA c the concentration of free radicals and in experiments with unicellular organisms (*Chlorella vulgaris*). In this experiment determined the effects of different concentrations of HA (15 samples) to the value of *Chlorella vulgaris* gross photosynthesis. These data are presented in table 2. They also show a stable correlation of physiological activity with the free radicals content in HA.

Conclusions

The results of our studies on the changes of composition and properties of SOM showed a significant evolution in the structure and functions of their HS, taking place at the burial of soils. A decrease in the total content of SOM in buried soils is accompanied by a sharp deterioration of its qualitative composition. In the molecular structure of HA increases the proportion of aromaticity, decreases the concentration of free radicals and physiological activity. The relationship consistently observed at different levels of organization of plant organisms and on isolated plant tissues (coleoptiles of *Maize*) and unicellular organisms (*Chlorella vulgaris*).