

## The role of lignin phenols in organic-mineral interactions in soils

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**Abstract.** The authors give a quantitative characterization of lignin phenols in soils and in particle-size fractions of grey forest soils (Russian Plane) and soils of the North Caucasus. Most of lignin phenols oxidation products (50 %) are associated with the coarse sand (>250 µm) fraction. However, in silty fractions (< 2 µm, 2-20 µm) there is a maximum of oxidation level and degree of transformation of the side chains of the lignin. The possible influence of soil mineralogical composition on the specific surface area of soil aggregates and on possible adsorption of lignin phenols is shown. Fe-Mn-concretions of all size contain the lignin of higher plants.

### Introduction

The complex aromatic structure and hydrophobic properties of lignin, as well as its high biochemical stability determine the unique role of this biopolymer in the processes of humification and organic-mineral interactions. However, this type of information is extremely limited. The purpose of the study is to identify patterns of intake, composition and transformation of lignin and its derivatives in different particle-size fractions and Fe-Mn concretions in soils of different zones.

### Materials and Methods

The chosen sites study included: light-gray forest soils (Grey Phaeozems Albic; Eutric podzoluvisols), light-gray forest gleyic and gley soils (Greyic Phaeozems Albic; Gleyic Greyzems) and gray soils of the southern taiga (Moscow district), as well as soils of vertical zones of Northern Caucasus

Lignin phenols were isolated using Amelung's version [1] of the Ertel-Hedges procedure [2]. The determination of lignin in the soils included the alkaline oxidation of the sample with copper oxide at 170°C under pressure in a nitrogen atmosphere, the precipitation of HAs, and the preconcentration of phenolic products on compact disposable C18 columns under pressure. Lignin preparations were isolated by the evaporation of ethyl acetate on a rotary evaporator. The phenol components of lignin were derivatized into trimethylsilyl ethers and separated on a gas liquid chromatograph-mass spectrometer (Hewlett-Packard, Palo Alto, CA, USA) with a flame ionization detector and a capillary column. Individual reaction products (vanillin, syringic aldehyde (al), syringic acid (ac), p-coumaric acid, and ferulic acid) were identified by comparing the retention times and peaks with those of the known components and amounts used as external standards. The reproducibility of results was 95%. The alkaline oxidation of vascular plant tissues and their remains by copper oxide in the soil yields 11 phenols [2], which can be grouped in accordance with their chemical nature into three structural families: vanillin (guaiacyl) (V), syringyl (S), and cinnamyl (C). Thus, the sum of oxidation products (VSC) reflects the total content of lignin in the sample. Determination of

carbon, nitrogen, sulfur is performed on element CNS analyzer (VARIO EL, Elementar GmbH, Hanau). Particle-size separation was made by ultrasonic method (Branson, 450W). The mineralogical composition of soil was investigated by x-ray diffraction (D5000 SIEMENS).

### Results and Discussion

Quantile distribution of lignin (VSC), the degree of oxidation (ac/al)v, the degree of lignin transformation in relation to the original plant tissue (T, %) in different particle-size fractions of soils of the Northern Caucasus and in gray soils of the Moscow region showed that with decreasing size fraction (< 2 µm, 2-20 µm), the amount of lignin in is decreased 10 times in comparison with the large fractions (20-250 µm, and >250 µm) (Fig. 1).

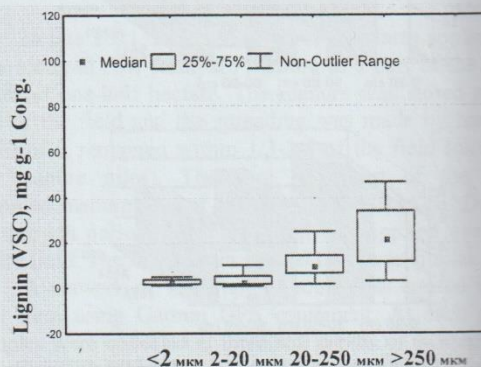


Figure 1. Statistical distribution of lignin (VSC), mg/g Corg., in particle-size fractions of soils studied.

Most of lignin phenols oxidation products (50 %) are associated with the coarse sand (>250 µm) fraction. However, in silty fractions there is a maximum of oxidation level (ac/al)v and degree of transformation of the side chains of the biopolymer (T,%) therefore, low values of S/V-relations, which are due to selective loss of syringyl aromatic structures, and demethylation of methoxyl groups, (check this sentence). Thus, in small fractions (<2 µm, 2-20 µm), maximum destruction of lignin phenols is observed. In the finer fractions the highest content of biophilic elements: carbon, nitrogen,



sulfur, due to microbial resynthesis is also observed. In the large fractions poorly decomposed residues enriched in lignin, are accumulated, whereas the fine fractions of soils are dominated by products of microbial activity. The higher degree of lignin phenols oxidation level on the surface of the aggregate than inside of it, leads to a higher ratio of acid/aldehyde (Ac/Al). These facts are in agreement with that the destruction of lignin occurs in the aerobic conditions. In the reductive zones, lignin weakly decomposes and its relative accumulation occurs, as in Ap horizon of Gleysoils [3].

Adsorption of lignin phenols on the mineral surface is facilitated by a high specific surface area of the mineral phase and its positive charge. Biopolymer molecules are encrusted with clay minerals and become inaccessible to microorganisms. Probably, this is the reason for the high correlation of the content of lignin oxidation products with the value of the specific surface area. The correlation coefficient ( $P = 0.95$ ) between the values of the degree of oxidation level and the specific surface area ( $m^2/g$ ) in light gray soils of the Kolomna Opole is about 0.97. The high values of the specific surface area are due to the presence of clay minerals: groups of illites, groups of vermiculite and mixed-layer minerals (Illite-montmorillonite), groups of kaolinite. It can be assumed that oxidized monomers of lignin are fixed by clay minerals.

The "ideal" matrix for adsorption of lignin phenols and enzymes are amorphous hydroxides of Fe and Al. They are widely distributed in the soil in the free form or in the form of Fe-Mn nodules [7]. Possessing a large specific surface, the lignin compounds become the center of further concretions formation. Indeed, it was shown that nodules of all sizes (>100 samples) contain the lignin of higher plants [3, 4]. In concretions from light grey soils the content of lignin oxidation products is 10 times less than in fine-grained soils, however, the content of acids exceeds that of aldehydes. The degree of lignin transformation in relation to the original plant tissues (T, %) in ferro-manganese nodules increases by 4 times (Table. 1). As a result, the molecules of humic acids in Fe-Mn-nodules have twice the aroma in comparison with humic acids of soils. However, the number of carboxyl structures in humic acids of concretions is two times higher than in the humus of soils. Perhaps these fragments

of the molecules increase the share of fulvic acids in the group composition of humus of concretions, according to the group and fractional composition of humus [6].

**Table 1.** The lignin content (VSC) in soils and Fe-Mn-nodules,  $n=5$ .

Gleysoils Mollic	Lignin (VSC), mg g <sup>-1</sup> Corg	Vanillic acids/vanillin (Ac/Al) <sub>v</sub>	Syringic acids/ syringaldehyde (Ac/Al) <sub>s</sub>	T, %
Ap, 0-15 cm	11.9	0.2	0.4	5.8
Fe-Mn Nodules (1-5mm)	1.3	0.6	1.4	20.8

Therefore, the oxidized monomers (and possibly oligomers) of lignin, as well as lignin phenols, become a part of humic acids [4, 5, 6]. The processes of interaction of lignin phenols with fine soil fractions play a key role in the stabilization of biopolymer and the formation of stable aggregates..

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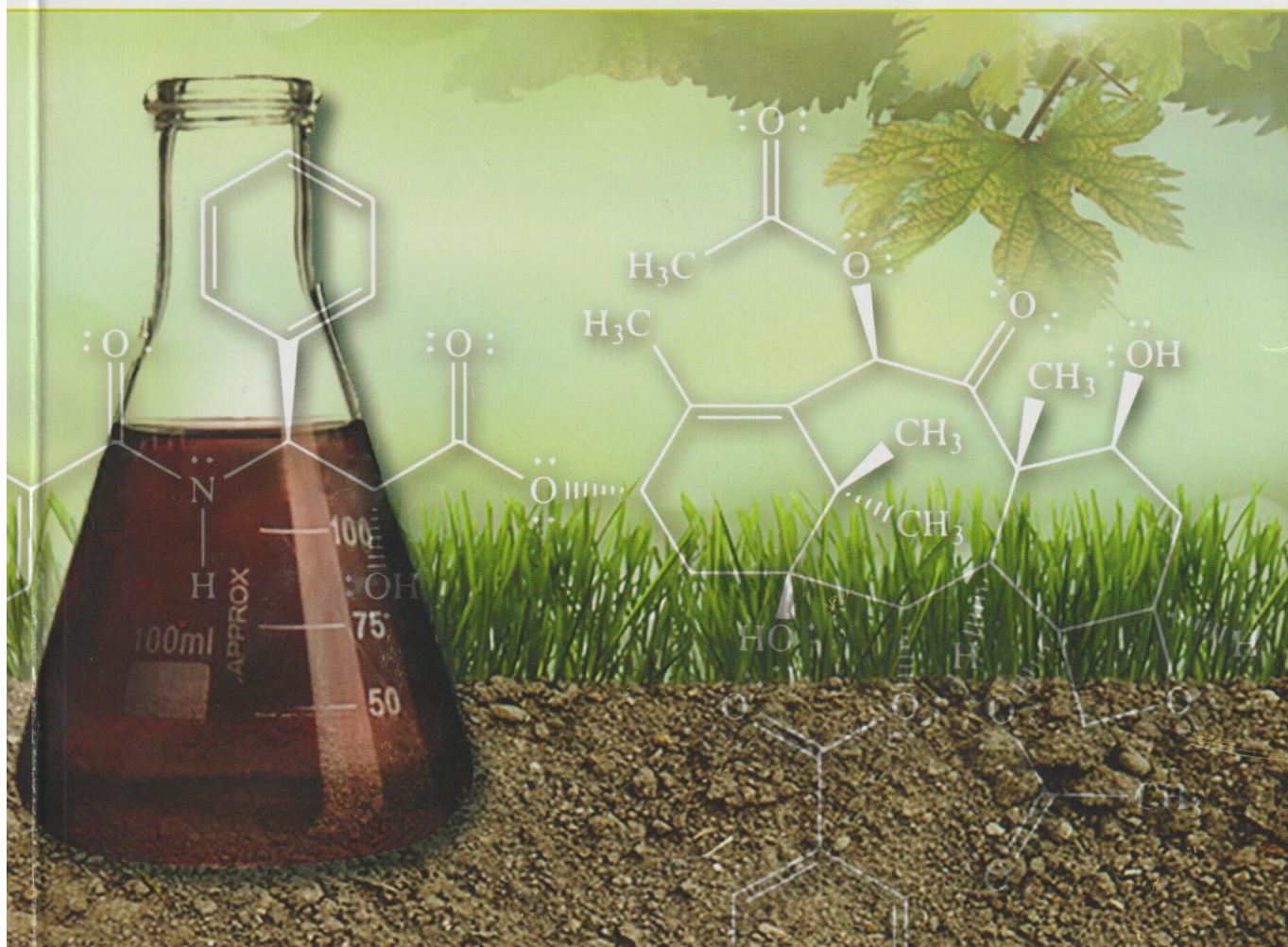


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