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Research Article

Humus and Humic Acids of Luvisol and Cambisol of Jiguli Ridges, Samara Region, Russia

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Luvisols and Cambisols are two types of sub-boreal soils, which are known as continental and humid-ocean types of soils in deciduous forests respectively. Morphological features of soil, which are frequently used as the main argument in solum diagnostics, are subjective and do not give final decision that continental Cambisols are a specific type of soils different from Luvisols. These soils were studied in a mountain massive—Jiguli ridges of Samara region, Russia, East European part. Humid climate of northern slopes leads to formation of brown type of humic acids (HA), while the conditions of eastern slopes assist to formation of gray HA. These HAs of different soils are different in elemental composition (C and N are higher in Cambisols, O is higher in Luvisols), carbon species according to 13-C NMR (aromaticity is higher in Luvisols, while the aliphatic, carbonylic and carboxylic compounds are higher in Cambisols). Cambisols are characterized by dominance of fulvic acids (FAs) on HAs, while the ratio of HA to FA groups in Luvisols is about 1,0. Essential differences in humus composition and humic acids properties confirm that local humid climate in continental forest-steppe leads to formation of Cambisols instead of zonal Luvisols.

1. Introduction

Deciduous forest soils of subboreal zone on the Russian plain are represented by Brown soils (Cambisols) and Gray—Dark Gray soils (Luvisols) [1]. These two soils form in warm semi-arid climate with annual air temperature of about 3–7°C, predominance of broadleaf plant species, on neutral or alkaline parent materials [2]. Usually, Luvisols are typical for plains, with dominance of alkaline loess-type parent materials in continental parts of subboreal zone. Cambisols are more typical for those parts of the Russian plain that are characterized by humid oceanic climate (Crimea, Carpathians, Caucasis, etc.), and the formation of these soils is usually connected with the mountain type of ridge relief and clay-textured mountain debris—deluviums or good-weathered eluviums.

The main differences between conditions of soil formation are climate and parent materials. On the scale of Russian plain Cambisols are typical for western part, while Luvisols are typical for the central part of the Russian plain. Soil combination on the territory of one landscape region is very untypical and can be revealed only in case of mountain regions, characterized by slopes of different exposition. Such type of soils' combinations were revealed in Samara Jiguli ridges, where Cambisols and Luvisols were formed on different slopes. These two soils are different in morphology, clay fraction chemistry, and mineralogy and are supposed to be very different in content, distribution, and composition of soil organic matter.

The geography of these Cambisols and Luvisols on the central part of the Russian plain is problematic and causes the discussion on the possibility of Cambisol's presence in continental part of forest-steppe zone with some deviations of local climate. This discussion started in 1970–1980 and hasn't finished yet [2]. The reason of this discussion consisted in the fact that morphological features of soils were used as a main argument in the determination of this type of soil. These features do not provide sufficient proof that continental Cambisols are a specific type of soils different from Luvisols. That is why this problem can be solved only on the base of detailed investigation of humus, which is known as soil component, strongly influenced by climate and the type of pedogenesis.

Cambisols are known as soils with prevalence of fulvic acids and dominance of alkylic-C carbon species in molecules with essential part of low molecular part [3]. Luvisols are different from Cambisols in mechanisms of soil organic matter stabilization due to different types of mineralogical profiles [4]. Luvisols are also known as soils with a high portion of aromatic carbon species [5].

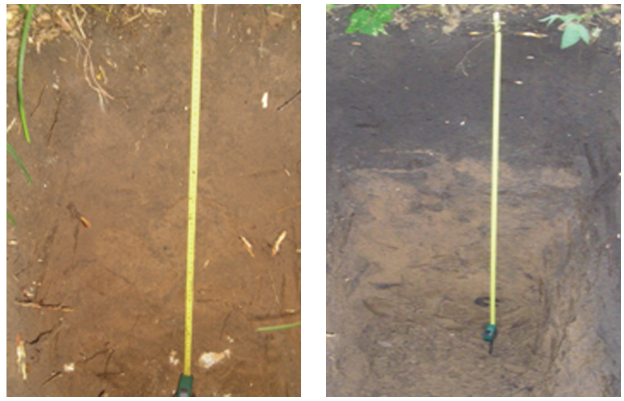
The objective of this study was to reveal differences in soil organic matter and humic acids properties of Cambisols and Luvisols in order to determine if the Cambisols are really different from Luvisols and thus give additional arguments, which could enable us to treat Cambisols as a specific soil type in the central part of the Russian plain.

2. Material and Methods

2.1. Description of the Study Sites. Jiguli ridges are situated in Samarskaya Luka, Samara Region, Midlle Povolgye, Russian plain. These ridges were formed in Pliocene and now their maximal height is 371 m. Now these ridges are a part of a protected area—Jiguli State Reserve, which is characterized by unusually high diversity of soils, presented by Cambisols, Luvisols, Rendzic Leptosols, Chernozems, and Albeluvisols. This diversity is caused by both great spatial heterogeneity of parent materials and redistribution of precipitation and insolation on slopes of different expositions.

Climate of Samara Ridges is classified as continental [6] with sharp differences, caused by slopes' expositions. Thus, the eastern and western slopes are exposed to dry, cold, and well-drained mountain valleys. There are no southern slopes, because this part of mountains passes into the Plateau of Samarskay Luka. The northern slopes are exposed to the Volga River—the biggest water reservoir in European Russia, and therefore climate here is warm, humid of marine type [6]. Annual precipitation is 620 and 570 mm, average temperature in January is -10°C and -21°C, for northern and valley-exposed (eastern and western) slopes, respectively. Annual air temperature is 4.8°C, average June temperature is $+20^{\circ}$C for both types of landscapes. According to Kudinov [6] Volga affects the northern slopes by decreasing climate continetality, increasing air humidity, and providing relatively uniform climatic conditions throughout the year.

The soils investigated (Figure 1) belong to two catenas. The first one is catena of the northern slope, where Cambisols (A-BW-Cca) on the slope foot are changed by Rendzic Leptosols on the slope crest. The second catena is



(a) (b)

Figure 1: Morphology of two soils investigated: (a) Cambisol and (b) Luvisol.

on the eastern slope, where the foot soil is Luvisol (A-EL-BT-Cca), changed by the same type of Rendzic Leptosols on the crest. Full-profile foot-slope soils, that is, Cambisols and Luvisols, are formed on clay-textured brown-colored debris, with the portion of stones about 15%, the portion of clay about 40%, the percentages of $CaCO_3$ about 2%–6%, with predominance of kaolinite (32%), illite (21%) and very low portion (10%) of montmorilonite in clay minerals composition.

The vegetation cover is represented by lime (*Tilia cordata*) forests with maple (*Acer tatarícum*) in lower layer on the first catena and lime-birch (*Betula pendula*) mixed forest on the second one.

2.2. Soil Sampling and Humic Acids Preparation. At least 3 soil pits were used for each type of soil for soil morphology description, determination of soil taxonomy, and sampling of individual samples. Soil pits were made according to detailed soil map of slopes; it means that 3 pits for each type of soil were made in one polypedon. Then, in laboratory, 3 or 4 individual samples of each horizon were mixed and homogenized. These samples of soil horizons of Cambisol and Luvisols with related profiles of Rendzic Leptosols in catenas were dried, grounded, and sieved through 2-mm sieve.

Humic acids (HA) powders were isolated according to IHSS standart method.

2.3. Methods of Organic Matter Analyses. The total organic carbon content was determined by Tuyrin dichromate-oxidation method (almost the same as Walkey and Black method); total nitrogen was measured in accordance with [7]. The group and fractional composition of humus was determined according to Ponomareva and Plotnikova procedure [5], which allows to calculate the CHA/CFA (humic to fulvic acids) ratio as well as the content of free, Ca and clay mineral-bonded groups of HA and FA, marked as 1, 2, and 3rd fractions, respectively. The ratio CHA/CFA is a ratio of carbon content of all HAs to carbon content of all FAs in soil. This ratio enables us to determine the so-called "humus types"—the degree of predominance of FA over HA or HA over FA.

According to this procedure [5] the fraction 1 was extracted by 0.1 M solution of sodium hydroxide. After this extraction the soil was decalcinated by hydrochloric acid with subsequent removing chloric ions by water. Then fraction 2 was extracted by the same sodium hydroxide solution. Fraction 3 was obtained by boiling the rest of soil in 0.02 M sodium hydroxide for 6 hours in special Koch boiler. Humic acids were separated from fulvic acids, being precipitated by sulfuric acid in all fractions: 1, 2, and 3. Summarizing the portions of HAs of 1, 2, and 3 fractions we got the value of CHA. The calculation of CFA was made in the same way.

The elemental analysis of HA was conducted on 185B-Hewlett Packard analyzer. Data was corrected on water and ash content.

The C-13-NMR spectra were registered on Brucker Ultra-Shield spectrometer with TMSPNA as a standard in liquid state.

3. Results and Discussion

3.1. Soil Diagnostics. The thickness of humus-accumulation horizons in Cambisol was 15 cm; the horizons were brown-colored, with high porosity, and overlaid by thick forest floor, which consisted of good expressed L and F subhorizons with total thickness of about 5 cm. Luvisol profile revealed the short forest floor—about 2.5–3.0 cm, underlaid by thick (25) dark-gray-colored humus horizon.

The middle parts of the two profiles were also different, that is, BW horizon of Cambisol was characterized by light-brown color, increased density in comparison with over- and underlayed horizon, and absolute absence of cutans. A layer of Luvisol is changed by EL—eluvial bleached horizon with abundant spots of silica accumulation; the lower transitional layer contains siltans, skeletons, and argillans, and leached spots of eluviation. This transitional part was underlayed by BT—clay-illuvial horizon with abundant agrillic cutans.

The main differences identified by soil macromorphology are the dominance of local weathering process in Cambisol and prevalence of eluvial-illuvial differentiation of soil profile in Luvisol. There was also morphological evidence of higher intensity of humus accumulation in Luvisol as compared to Cambisol. This is frequently explained by a more intensive development of humification process in dry and continental conditions, while the wet and humid climate assists to formation of acid-brown-mull humus with low degree of humification [3, 5].

3.2. Carbon Content and Distribution. Total stock of fresh forest floor identified as L horizon is estimated as 340 and 22 g/m^2 for Cambisol and Luvisol, respectively, while the stock of organic matter in fermentation (F) subhorizon was estimated as 351 and 280 g/m^2. The root stock was estimated as 124 and 88 g/m^2 for these soils. This data shows that Cambisol is characterized by slower processes

Table 1: Total carbon content, portion of HAs, humus type ratio and humus richness by nitrogen.

Horizon	Ctotal, g/kg	$\frac{\text{CHA}}{\text{Ctotal}}$	$\frac{\text{CHA}}{\text{CFA}}$	C/N
		Cambisol		
A	37.0	19.	0.66	15.5
AB	10.2	18.6	0.38	19.9
BW	3.4	23.6	0.61	6.6
		Rendzic leptosol related to cambisol		
A	38.0	26.4	1.10	16.7
		Luvisol		
A	49.0	18.0	0.86	12.3
BEL	3.6	25.0	1.00	18.0
BT	4.6	38.0	1.04	8.2
		Rendzic leptosol related to luvisol		
A	37.6	31.3	2.31	14.5

of mineralization and humification of organic matter as compared to Luvisol.

The absolute total content of organic carbon (Table 1) is higher in Luvisol than in Cambisol, which confirms the fact of bigger intensity of humus accumulation process in the former. Also the C/N ratio is less in Luvisol, which is the result of more intensive humification and mineralization in this soil; it was also reported as a typical difference of Luvisols from soils of humid climates [5].

The profile distribution of humic acids was more or less gradual in Cambisol solum, while it decreases sharply with depth in Luvisol. Previously it was shown that if HA portions increase with depth, then some migration of HA is possible [8], presumably in complexes with clay minerals. This suggestion can be confirmed by the morphology of agrillic cutans in BT horizons, which is characterized by mixed humus-clay composition of agrillic material. The CHA/CFA ratio, which is known as index of humus type [9], classifies Cambisol as a soil with predominance of FAs, while Luvisol was identified as a soil with prevalence of HAs. This fact also substantiates the soil diagnostic conducted on the base of morphological properties and shows an essentially higher humification degree in Luvisol.

The same differences were revealed for Rendzic Leptosols of ridges crests related to Cambisol and Luvisol in catenas. The data in Table 1 confirms the hypothesis that different slope expositions affect also the properties of "lithogenic" soils, that is, Rendzic Leptosols. Those of Leptosols, which are formed on the northern-exposed slopes, were close to Cambisols in humus characteristics, while the valley-exposed slopes contain Leptosols with well-humified organic matter, lower C/N ratio, and higher portion of HAs to Ctotal, which makes it close to Luvisols.

3.3. Humus Fractions. According to the classification of HAs by Tuyrin [1937] all the HAs can be divided into three fractions: free, Ca-connected, and clay minerals connected. The portions of HAs fractions are different in the soils investigated. Cambisol is characterized by low content of

Table 2: The groups of HAs in soils: Percentage of humic acid carbon to total C content.

Horizon	Forms of HAs		
	Free	Ca-connected	Clay-connected
Cambisol			
A	4.0	7.8	7.8
AB	2.9	9.8	5.9
BW	5.9	5.9	11.8
Rendzic leptosol related to cambisol			
A	10.4	5.3	10.7
Luvisol			
A	2.8	8.9	6.3
BEL	1.0	16.0	8.0
BT	2.0	35.0	26.0
Rendzic leptosol related to luvisol			
A	1.6	18.6	11.1

Table 3: HA elemental composition.

Element content, atomic, %	Cambisol	Luvisol	RL related to Cambisol	RL related to Luvisol
C	36.97 ± 0.07	34.34 ± 0.16	38.16 ± 0.26	36.23 ± 0.24
H	37.25 ± 0.08	38.78 ± 0.12	35.78 ± 0.13	38.53 ± 0.23
N	2.89 ± 0.30	2.03 ± 0.45	2.48 ± 0.34	2.75 ± 0.27
O	22.88 ± 0.25	24.84 ± 0.32	23.57 ± 0.27	22.48 ± 0.34
C/N	12.79	16.92	15.39	13.17
H/C	1.00	1.13	0.94	1.06
O/C	0.62	0.72	0.62	0.62

Table 4: Carbon species of humic acids on the base of 13-NMR spectra, Percentage of each carbon species to carbon in molecule.

Carbon species	Cambisol	Luvisol	RL related to cambisol	RL related to luvisol
Aromaticity	0.6	0.7	0.6	0.7
Aromatic C	29.4	42.3	23.4	34.9
Aliphatic C	18.9	13.3	18.2	18.4
Carbonylic	5.8	4.4	3.5	3.4
Carboxylic	20.3	16.8	17.5	18.8
Phenolic	6.9	7.7	5.3	7.7
Aldehyde	19.1	16.0	32.9	17.0

free HAs with approximately equal portions of Ca and Clay-connected ones. The profile distribution of these fractions is uniform and does not show the illuviation and migration pattern. Luvisol shows the prevalence of Ca-connected fractions of HAs, which are typical for these soils [5]. The portion of this fraction increased with depth, which is the result, and an index of intensive illuvial process. Ca-connected HAs are wellknown as “dark” type of HAs, typical for continental types of climate of forest-steppe and steppe regions. Therefore, HAs in the Luvisols studied are typical for forest-steppe conditions also in terms of its migration ability in profile and its preference in reactions with calcium. The Leptosols, thus related to Cambisols and Luvisols, show the same proportions of fraction as soils to which they are related on the slopes.

3.4. Humic Acids Elemental Composition. The difference between soils in HAs elemental composition (Table 3) was statistically significant only in case of carbon (Cambisols with related Leptosols show higher content of C in comparison with Luvisols and related Leptosols) and hydrogen (which is on the contrary higher in Luvisol and related soils than in Cambisol). The differences between nitrogen and oxygen content are not statistically significant. This data of elemental composition only gives a possibility to classify these substances as HAs according to classification of Orlov [9] but does not reveal the essential difference in its elemental composition.

3.5. 13-C NMR Spectra of Humic Acids. On the base of 13-C NMR (Table 4) HAs of Luvisol on eastern slopes are more aromitisized, and contain less aliphatic carbon and a smaller part of carbonylic, carboxylic groups, and aldehydes. The same tendencies were revealed for HAs extracted form Rendzic Leptosols genetically connected in catenas with Cambisols and Luvisols. Luvisols and related Leptosols show higher aromatic carbon, essentially less aldehyde groups, and equal aliphatic carbon species portion. Therefore, the differences between Cambisol and Luvisol related to Leptosols are less than HAs of these full profile soils. In all cases we can conclude that HAs of soils on valley-exposed slopes are more aromatic, that is, more humified as well, which is in good correspondence with the data of humus type and the percentage portions of HAs to C total.

4. Conclusions

Russian steppe and forest steppe are usually considered as plain-type macrolandscapes with continental climate with dominance of Chernozems in steppes and Luvisols in forest-steppes. These soils are characterized by dark-colored humus accumulative horizons, prevalence of well-aromitisized HAs of "dark type" [10], which is frequently connected with Ca and partially able to migrate in soil profile, especially in forest soils. The Brown soils or Cambisols are very unusual in the central part of the Russian plain and were found only in the Ural and Jiguli ridges. The first investigation of Jiguli Cambisols has revealed that this type of soils was previously identified correctly and its formation is caused by wet humid climate of northern slopes of Jiguli ridges, which are known to be under thermoregulation influence of Volga river basin. The HAs of these Cambisols are very different from HAs of Luvisols. The main differences are lower aromaticity and higher aliphaticity of Cambisols HAs. At the same time smaller speed of humus accumulation with dominance of FAs in group humus composition and absence of illuviation process in these soils gives evidence that humification in soils of northern slopes is totally different in all parameters from the humification in soils of valley-exposed slopes.

The main result of this paper is the demonstration of the fact, that humid climate assists in the formation of Cambisols, which are ocean type of soils, even in central part of the Russian plain, which for the first time gives evidence of radical changes of humus and humic acids type.

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