

Organic Matter and Elemental Composition of Humic Acids in Soils of Urban Areas: The Case of Rostov Agglomeration

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Abstract. The aim of investigation was to evaluate the effects of urbanization on the organic matter of urban soils in the South of Russia.

The type of vegetation has an impact on the amount and quality of soil humus. In soils of the forest-park area of the city, an increase of humus content in the upper 10-cm layer to the average value of $7.5 \pm 0.63\%$ has been observed, which is significantly higher than the humus content of arable chernozem surrounding the city (3.5–4%).

The humus profile acquires the features of the forest soil. Reduction of humus content is characteristic of buried and sealed soils. The structure and composition of humic acids is largely due to the type of anthropogenic impact. However, regardless of the nature and degree of changes, the transformation of HA molecules are within the defined soil type. The most significant changes are noted for HA from Calcic Chernozem of the forest park. The significant decrease in humus content in urban soils is due to a change of soil conditions. The fact that humic acids of chernozem are less benzenoid and characterized by more advanced peripheral portion of the molecule, with a higher degree of enrichment with nitrogen and sulfur. Sealing the soil under the asphalt leads to the development of HA oxidation and hydrogenation processes. The reduced participation of aromatic moieties in the molecules of HA in the horizon UR of Ekranic Technosol has been noted.

Keywords: Calcic chernozem · Ekranic technosol · Humic acids · Soil organic matter · Urban pedogenesis · Urban soil · Urbic technosol molic

1 Introduction

The study of soil organic matter is a necessary step to solve many issues related to the rational use of soil resources and forecasting the consequences of urban pedogenesis. It is also needed to create the theoretical basis for soil monitoring [13, 15, 17, 29]. The humus substances play a leading role in the formation of a soil body. On one hand, they possess substantial dynamism and capacity to respond to any changes in the environment or to human intervention, and on the other, they are sufficiently “conservative”

moieties capable to resist a certain level of disturbing influences, maintaining the ecological status [3, 5, 7, 14, 16, 22, 25, 28, 35].

According to modern concepts, humic acids, the main component of the humus, are a system of high-molecular compounds, and their elemental composition is an average of chemical elements concentration in a group of chemically close, but at the same time, structurally different substances included in the system. However, it was found that the elemental composition of humic acids naturally changes from one type of soil to the other [1].

Orlov [19, 20, 22] has shown that the distribution of carbon in humic acids of the same soil type is approximated by the normal distribution law, with varying rates depending on the type of soil. This allowed him to make a conclusion that humic acid is not a random mixture and its composition depends on the pedogenic conditions. Thus, it was proved that the determination of the elemental composition of humic acid is a necessary stage of research in the study of soil humus status of any soil. There is no doubt, that many other informative methods to study the molecular structure of humic acids exist, but the elemental composition still remains one of the main, and only the significant labor intensity explains the relatively rare use of such a method in the works. However, it is possible to find some information in the literature on the elemental composition of humic acids of various soil and peat types in their natural state [9, 18]. At the same time, such characteristics of technogenically transformed and urban soils are absent. Urbanized areas are characterized by varying degrees of disturbance and anthropogenic transformation of soil [2, 11, 12, 30, 31]. Previously, the significant features of humus composition in urban soils were found [2, 10, 32, 38], therefore the analysis of the elemental composition of HA in these objects also seems to be of particular importance.

Humic acids are substances with irregular chemical composition and structure, characteristic of polydispersity and structural elements heterogeneity [8, 25, 36, 37]. According to Orlov [20], the coefficients of variation of the carbon content in the humic acids obtained from the same type of soil reach 5–8%, which often exceeds the differences between the genetic types. The classic pattern of HA carbon content change in the zonal aspect manifests itself only in average values. His works have shown the average carbon content of the humic acids of main soil types. In particular, in Chernozems the average carbon content is 57.9%, and the variation limits are 52.0–63.8% (in terms of dry ash-free matter).

The aim of the study was to study the composition and structure of humic acids of Chernozem soil under various degrees of anthropogenic impact of the Rostov agglomeration.

2 Materials and Methods

2.1 Description of Field Experiment and Sampling

Rostov agglomeration is a part of the South-Eastern district of Rostov region, occupying about 40% of its territory, and it is strongly monocentric. The total population of the agglomeration is more than 2 million people, the population density – 147 people

per square kilometer. Agglomerations are characteristic of an intensive process of adjacent territories development, called suburbanization [34]. As a result, over the past two decades, the city of Rostov-on-Don has de facto merged with Aksay and Bataisk cities.

With consideration for the complex nature of the object under study, 65 soil profiles were established in different regions of the Rostov agglomeration, in which the humus status was studied. The studies were conducted in two periods: 1996–2001 and 2010–2015. When studying the natural soils, the profiles were laid in park and recreational areas of the city and in arable areas adjacent to the edge of the city. As a rule, they are Calcic Chernozem and Calcic Chernozem Aric soil types. The rest of the soil profiles are confined to the industrial and residential areas and represent anthropogenically transformed soils (Ekranic Technosol, Urbic Technosol Mollic and Calcic Chernozem Novic Technic). The cultivated black soil (Calcic Chernozem Aric) of the city outskirts and of the Botanical Garden (Southern Federal University), which occupies an area of 160 ha in the geographic center of agglomeration (Fig. 1) were chosen as a comparison object for the artificial forest park soils and for soils with varying degrees of anthropogenic transformation.

In the elemental composition study of the humic acids of urban soils in Rostov agglomeration, we can only refer to previously analyzed humic preparations, but cannot use them as a reference sample. In this regard, aiming for the purity of our experimental design, the preparations of humic acids were made from the horizons of Calcic Chernozem Aric adjacent to the city as well as from urban soils in Rostov-on-Don, identified as the most typical.

Thus, the selected soil types were as follows: (i) Calcic Chernozem, located in the “protective” forest park zone of Rostov-on-Don. This soil is experiencing the impact of woody vegetation uncharacteristic of natural steppe conditions; (ii) Ekranic Urbic

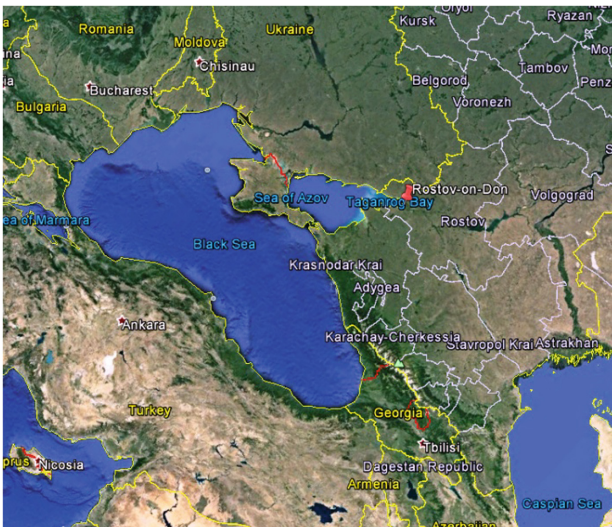


Fig. 1. Locations of soil profiles in Rostov agglomeration.

Technosol Molic, located in the historical center of Rostov-on-Don. This profile combined the asphalt sealed thick urbik horizon and subhorizons with a classic almost full-profiled chernozem, buried at a depth of 115 cm; and (iii) Calcic Chernozem, located in agricultural land within the borders of the agglomeration between the cities of Rostov-on-Don and Aksay. Naturally, arable land was also exposed to human impact, but compared to the urban soils these impacts were minimized and the soil did not experience overt influence of urban pedogenic processes.

2.2 Chemical Analysis

In the study of humus state the determination of organic carbon was conducted twice in the samples from each horizon by two essentially different analytical methods:

1. The wet combustion method was used for the determination of carbon content in accordance with method standardized in the Russian Federation (State Standard 26213-91),
2. Method of high temperature catalytic burning in total organic carbon analyzer TOC-L CPN Shimadzu, where the organic carbon (TOC) is determined as the difference between the overall total (TC) and inorganic (IC) carbon. The principle of total carbon (TC) determination is based on the direct burning of the sample in the TC combustion tube filled with an oxidation catalyst, and heated to 680 °C. Our studies have shown that the results obtained by the oxidation method and by the direct combustion on a Shimadzu TOC-L CPN analyzer are well matched: the differences between the methods lie within the determination error [2].

2.3 Humic Acids Extraction

Extraction of humic acid preparations (HA) was carried out by treating the soil samples with 0.1 N sodium hydroxide after decalcification by 1 N HCl. The isolated raw products were purified by dialysis in cellophane bags, followed by additional purification by electrodialysis. The suspension was then dried at 60 C [24].

Elemental analysis of the obtained HA preparations (i.e., content C, O, H, N) was made in the laboratory of analytical chemistry department, Moscow state university, on CHN-analyzer «Carlo Erba» model 1106, the sulfur content was determined in the Laboratory of Applied Soil Science of the University of Essen (Essen, Germany) on a similar instrument (Carlo Erba). The oxygen in HA preparations were calculated by difference. Elemental analysis data were recalculated to the ash-free sample.

The contents of the carboxylic and hydroxylic functional groups were determined by direct and back titration [24]. The use of a complex of HA isolation and purification methods yielded relatively low-ash products, which allowed to obtain high-quality IR spectra. The IR spectroscopy was carried out in the HA preparations isolated from Ad and A1 horizons of forest park Chernozem, Ap and A of arable Chernozem and UR1 and A_{bur.} of Ekranic Urbic Technosol Molic. The IR spectra of the HA were obtained using KBr technique on a two-beam-automatic infrared spectrophotometer IKS-29 in the range of 4200–400 cm⁻¹ [21].

3 Results and Discussion

3.1 Humus State of Urban Soils

The most typical 65 soil profiles were chosen for better representation of the changes in humus state of urban soils. They were combined into two groups depending on the level of transformation of their morphological characteristics:

- (i) Natural soils - Calcic Chernozem, Calcic Chernozem Aric
- (ii) Anthropogenically transformed soils - Ekranic Technosol, Urbic Technosol Molic and Calcic Chernozem Novic Technic.

The most informative data on total organic carbon content in natural soils and anthropogenically transformed soils of the city are presented in Tables 1 and 2.

According to primary research of the area which is now occupied by the Rostov agglomeration, average (from 27 sections) humus content in the 0–10 cm layer characteristic for Calcic Chernozem of the northern Azov region was 5.7% with a range

Table 1. Contents of total organic carbon in natural soils of Rostov agglomeration

Horizon	Horizon thickness, cm	C org., by wet combustion, %	Humus, by wet combustion, %	TC, %	IC, %	TOC, %	Humus, by TOC, %
1	2	3	4	5	6	7	8
Calcic Chernozem Aric (arable land, Aksay city, settl. Yantarny; profile 1205)							
Ap	0–25	2.62	4.52	2.42	0.01	2.41	4.16
A1	25–40	2.22	3.83	2.38	0.14	2.24	3.87
B1	40–60	1.48	2.55	2.34	0.76	1.58	2.72
B2	60–85	1.14	1.97	2.26	1.18	1.08	1.86
BC	85–110	0.68	1.17	2.30	1.72	0.57	0.99
Cca	110–130	0.57	0.98	2.27	1.81	0.46	0.80
Calcic Chernozem Aric (fallow, Rostov-on-Don city, Botanical Garden (SFedU); profile 1403)							
Ad	0–15	2.22	3.83	2.55	0.02	2.53	4.36
A	15–50	1.83	3.15	2.21	0.01	2.20	3.79
B1	50–65	1.54	2.65	2.13	0.33	1.80	3.09
B2	65–90	1.25	2.16	2.26	1.06	1.19	2.06
BC	90–110	1.03	1.78	2.39	1.88	0.51	0.88
Cca	110–150	0.40	0.69	2.08	1.93	0.15	0.26
Calcic Chernozem (forest park, Rostov-on-Don city; profile 1203)							
Ad	0–10	4.22	7.28	4.16	0.01	4.14	7.14
A1	10–50	2.68	4.62	2.58	0.00	2.58	4.45
B1	50–65	2.34	4.03	1.93	0.01	1.92	3.31
B2	65–90	1.65	2.84	1.29	0.02	1.27	2.18
BC	90–110	0.97	1.67	2.06	1.58	0.48	0.82

Table 2. Contents of total organic carbon in anthropogenically transformed soils of Rostov agglomeration

Horizon	Horizon thickness, cm	C org., by wet combustion, %	Humus, by wet combustion, %	TC, %	IC, %	TOC, %	Humus, by TOC, %
1	2	3	4	5	6	7	8
Urbic Technosol Molic (Rostov-on-Don city, residential part of the city; profile 1303)							
UR1	0–45	1.33	2.29	1.82	0.90	0.92	1.58
UR2	45–70	2.26	3.89	1.78	0.33	1.46	2.51
UR3	70–103	2.45	4.22	1.64	0.39	1.25	2.15
BC	103–130	0.66	1.13	2.05	1.50	0.54	0.94
Cca	130–170	0.50	0.86	1.65	1.32	0.33	0.57
Ekranic Technosol Urbic Molic (Rostov-on-Don city, residential part of the city; profile 1201)							
UR1	18–35	1.26	2.17	–	–	–	–
UR2	35–57	1.03	1.78	1.50	0.83	0.66	1.14
Abur	58–87	1.14	1.97	1.07	0.01	1.06	1.82
B1	87–107	0.97	1.67	1.01	0.01	1.00	1.73
B2	107–133	0.8	1.38	1.73	1.06	0.68	1.17
BC	133–160	0.8	1.38	1.97	1.61	0.36	0.62
Cca	160–206	0.28	0.48	1.61	1.39	0.22	0.38
C	206–280	0.40	0.69	1.37	1.20	0.17	0.29
Ekranic Calcic Chernozem Novic Technic (Rostov-on-Don city, residential part of the city; profile 1401)							
UR1	20–40	–	–	1.95	0.72	1.23	2.11
UR2	40–45	1.2	2.07	1.53	0.13	1.40	2.41
A	45–72	1.37	2.36	1.42	0.01	1.41	2.43
B1	72–92	1.08	1.86	1.02	0.02	1.00	1.73
B2	92–114	0.74	1.28	1.94	1.38	0.56	0.97
BC	114–132	0.51	0.88	2.16	1.92	0.24	0.42
C	132–182	0.28	0.48	1.98	1.83	0.15	0.26
D	182–240	0.06	0.10	0.19	0.05	0.14	0.24

from 4.4 to 7, 6%. Reduction of humus content with the depth was very gradual - from 5.7 to 1.7% at a depth of 100 cm [39].

Studies [10] have shown that an increase of humus content in the forest area is observed in the surface 10 cm layer. During the sixty-year period the humus content of $7.5 \pm 0.63\%$ ($n = 12$, $p = 0.95$) have become the average value for these soils varying from 6.5 to 10.0%.

On reserve lands (fallow lands and waste lands) and on agricultural lands surrounding the city the humus content of calcic Chernozems was in average $4.0 \pm 0.25\%$ ($n = 7$, $p = 0.95$). At the same time on the fallow plots compared to cropland some increase in humus content of the upper soil horizons has been stated.

Reduction of humus content is a characteristic feature of these soils that is well illustrated by the example of sealed soils [10]. Soils located under the asphalt are usually characterized by lower humus content, for instance in the sealed horizon A, which is covered with an impermeable coating contained only 3.5% of humus.

3.2 The Elemental Composition of Humic Acids

The elemental composition of humic acids, presented in a percent by weight (Table 3) has shown that the carbon content is within these oscillations $M \pm \sigma$, determined by Orlov [23]. The findings also confirmed the pattern established for the chernozems of the Rostov region previously: lower carbon content in humic acids as compared to the chernozems in other areas, which is due to the specifics of the provincial humification [4].

The nitrogen content of humic acids changes interestingly through the profile of the studied soils. The enrichment of humic acids with nitrogen is explicitly traced in the upper horizons of the soil under woody vegetation, whereas in arable and buried soils, this phenomenon is not expressed. There was also a slightly higher content of this element in the urbic horizon of Ekranic Technosol.

Humic acids of the sod horizon of Chernozems from park and recreational areas were enriched not only with nitrogen, but also with sulfur and hydrogen.

Table 4 shows the elemental composition of humic acids in terms of atomic percent. The distribution of humic acids carbon in the soil profile has a wavy character. In all three studied soils we noted the high content of this element in the B1 horizon.

Table 3. Elemental composition of humic acids in urbostratozems and chernozems of Rostov-on-Don, recalculated to an ash-free sample

Horizon	Sampling depth, cm	Humic acids; mass percent, %					
		C	H	O	N	S*	ash
Calcic Chernozem (park-recreational zone of the city)							
Asoc	0–10	52.05	4.19	38.96	4.80	0.60	0.56
A	10–25	54.89	3.69	37.21	4.21	0.37	6.02
B1	25–40	54.94	3.50	37.50	4.06	0.37	5.72
B2	40–60	52.65	3.50	39.95	3.90	0.30	3.52
Calcic Chernozem Aric (arable land at the outskirts of the city)							
Ap	0–25	54.48	3.45	38.59	3.48	0.25	3.80
As/p	25–55	54.59	3.34	38.62	3.45	0.22	3.24
B1	55–80	56.69	3.58	36.33	3.40	0.21	2.91
B2	80–105	49.11	3.76	43.53	3.60	0.18	11.40
Ekranic Technosol Urbic Molic (city centre)							
UR	95–115	53.57	4.0	38.4	4.2	0.29	3.47
A _{bur.}	115–140	50.74	3.4	42.2	3.7	0.21	2.97
B1	140–160	54.63	3.5	38.3	3.6	0.17	5.17
B2	160–175	52.40	3.2	40.9	3.6	0.20	2.59

Table 4. The elemental composition of humic acids and the degree of their oxidation in the Chernozems and Technosols Rostov-on-Don, recalculated to an ash-free sample

Horizon	Thickness, cm	Elemental composition, at. %				Atomic ratios				Ω
		C	H	O	N	H:C	O:C	(H:C) Rev.	C:N	
Calcic Chernozem (park-recreational zone of the city)										
Ad	0–10	38.45	36.86	21.67	3.02	0.96	0.56	1.86	12.71	+0.17
A	10–25	42.12	33.64	21.47	2.76	0.80	0.51	1.48	15.23	+0.22
B1	25–40	42.83	32.52	21.93	2.72	0.76	0.51	1.44	15.76	+0.26
B2	40–60	41.20	32.64	23.52	2.63	0.79	0.57	1.55	15.64	+0.35
Calcic Chernozem Aric (arable land at the outskirts of the city)										
A ar	0–25	42.75	32.20	22.69	2.35	0.75	0.53	1.46	18.16	+0.31
A u/ar	25–55	43.25	31.46	22.91	2.38	0.73	0.53	1.44	18.20	+0.33
B1	55–80	43.83	32.87	21.08	2.23	0.75	0.48	1.39	19.67	+0.21
B2	80–105	37.91	34.48	25.21	2.41	0.91	0.67	1.81	15.73	+0.42
Ekranic Technosol Urbic Molic (city centre)										
UR	95–115	40.07	35.76	21.47	2.70	0.89	0.54	1.61	14.87	+0.18
[A]	115–140	40.27	32.16	25.10	2.48	0.80	0.62	1.63	16.23	+0.45
B1	140–160	42.68	32.46	22.42	2.44	0.76	0.53	1.47	17.50	+0.29
B2	160–175	42.04	30.95	24.69	2.32	0.74	0.59	1.53	18.17	+0.44

In profile distribution of HA nitrogen there is a clear tendency to reduction of the nitrogen content with depth, both in chernozems of recreational part of the city, and in sealed soils.

The oxygen content of humic acids varies. The calculation of the degree of humic acid oxidation by the method of DS Orlov [19] has shown that in all horizons of the studied soils the humic acids are present in reduced form, but the changes in the degree of oxidation through the profile are not the same. Humification process is characterized by an increase of the oxidation degree in the formed products [23], and it is clearly seen in the Chernozems of the recreational area. A gradual increase of this index is noted down the profile with a minimum content in the horizon Ad. At the same time, in sealed and arable analogues the pattern is different: there is a “jump” of the degree of oxidation from the horizon B1 to the horizon B2, where it is much higher than in the other layers.

3.3 The Optical Density of HA

The optical density of the humic acids in studied soils is characterized by the data presented in Table 5. The lowest values of HA optical densities were recorded in the Chernozem of forest park in the surface humus-accumulative horizons Ad and A. At the same time the results of functional groups determination have shown that these horizons are characterized by the highest presence of hydroxylic and carboxylic groups. These low values of the optical density are also observed in the UR horizon of Ekranic Technosol, although high values of neither COOH nor OH groups have been recorded in this horizon during the study.

Table 5. The optical density, color coefficients and the functional groups in Chernozems and Technosols of Rostov-on-Don

Horizon	Sampling depth, cm	0.001% E 1 cm	E _{465/650}	E _{400/500}	E _{500/600}	E _{600/700}	COOH	OH
							g-eq/100 g	
Calcic Chernozem (park-recreational zone of the city)								
Asod	0–10	0.07	3.16	2.04	1.85	1.88	0.620	0.360
A	10–25	0.08	2.90	1.89	1.74	1.83	0.632	0.376
B1	25–40	0.11	2.87	1.89	1.74	1.81	0.420	0.179
B2	40–60	0.10	2.84	1.83	1.74	1.83	0.444	0.206
Calcic Chernozem Aric (arable land at the outskirts of the city)								
Ap	0–25	0.10	2.90	1.86	1.74	1.88	0.408	0.235
A _{s/p}	25–45	0.12	2.91	1.84	1.74	1.90	0.434	0.235
B1	55–80	0.10	3.04	1.87	1.78	1.97	0.439	0.251
B2	80–105	0.07	3.10	1.89	1.82	1.98	0.300	0.460
Ekranic Technosol Urbic Molic (city centre)								
UR	95–115	0.09	3.04	1.89	1.79	1.92	0.365	0.176
A _{bur.}	115–140	0.11	2.63	1.82	1.66	1.73	0.384	0.137
B1	140–160	0.11	2.97	1.88	1.77	1.89	0.424	0.258
B2	160–175	0.10	3.07	1.91	1.79	1.93	0.415	0.193

In the lower, natural horizons the pattern of changes in optical density values of the HA is similar to what is seen in ordinary calcic Chernozem (arable land on the outskirts of the city).

Down through the soil profile the optical density of HA decreases and the color factor increases respectively. The highest E4: E6 value is typical for the sod horizon.

3.4 The IR Spectra of Humic Acids

IR spectra of the studied HA preparations represent a practically identical set of medium intensity bands (Fig. 2), slightly varying in their ratio in the individual soil profiles, with peaks at 3390 (3375), 2925 and 2865, 1710, 1620–1605, 1395, 1245 (1225), 1045, 520 and 465 cm^{-1} . In addition, in the individual spectra ledges, kinks or bands of a very weak intensity are detected at 3195 (3210), 3075, 2550, 1695, 1665, 1650, 1090, 915, 800, 765 cm^{-1} .

Humic acids IR spectra of the two upper genetic horizons of arable Chernozem are almost identical in a set of absorption bands, as well as in their intensity. In the short-wavelength range there is a broad band at 3390 cm^{-1} (stretching vibrations of OH groups of various kinds, linked by hydrogen bonds), in its long-wavelength wing there are bands of a weak intensity at 2926 and 2865 cm^{-1} (stretching vibrations of CH groups in CH₂).

In addition, in the horizon Ap a very weak peak at 3225 cm^{-1} may be noted, which is perhaps characteristic of the valent NH group involved in hydrogen associated interactions, and 3075 cm^{-1} , which determines the presence of the aromatic CH groups having no more than 2–3 substituents in the structure. Weak absorption at 2550 cm^{-1} is

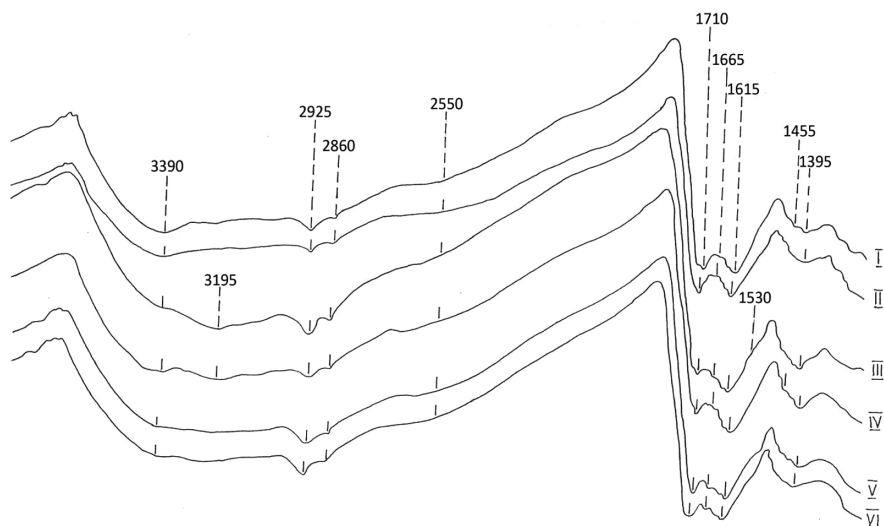


Fig. 2. IR spectra of humic acids of natural and anthropogenically transformed soils of the city (the range of 4200-1200 cm^{-1}): I, II – Ap and Ap1 horizons, (Calcic Chernozem Aric, arable land on the outskirts of the city); III, IV – Ad and A horizons (Calcic Chernozem, park and recreational areas of the city); V, VI – UR and Abur horizons (Ekranic Technosol Urbic Molic, city center).

due to carboxylic acids, more exactly with the OH groups of carboxylic acid dimers. The absorption band of carboxyl groups ($\text{C} = \text{O}$ of COOH) is comparatively intense and well defined at 1710 cm^{-1} and in the long-wavelength region at 1240 cm^{-1} ($\text{C}-\text{O}$ in the COOH). Another band at $1610\text{--}1620 \text{ cm}^{-1}$, which is associated with the appearance of the $\text{C} = \text{C}$ benzenoid structures is comparable to the intensity of the absorption band of the carboxyl groups. In the same interval in the humic acids of the Ap horizon there is a weak peak at 1660 cm^{-1} attributable to $\text{C} = \text{O}$ quinone linked hydrogen bond, and (or) characterizing the expression of $\text{C} = \text{O}$ groups in the COOH of the aromatic ring.

In the long wavelength region of the spectrum there are absorption bands at $1045\text{--}1035 \text{ cm}^{-1}$, 525 and 465 cm^{-1} (Ap horizon), which are due, basically, to the presence of Si-O clay minerals, and in the horizon A1p, there are weak intensity bands at 1095 cm^{-1} , 800 cm^{-1} besides the above-mentioned bands. They are also due to the presence of silicates in the HA samples.

The IR spectra of humic acids isolated from forest park soils were characterized by following differences. The absorption band of carboxyl groups (1710 cm^{-1}) is less intense than in the HA of the arable Chernozem, and it is typical both for HA of the upper and lower horizons of this profile. Furthermore, an increased intensity of various OH groups absorption bands at $3375\text{--}3390 \text{ cm}^{-1}$, and possibly also NH-groups, should be noted because a separate absorption band appears in this range at $3195\text{--}3210 \text{ cm}^{-1}$, characteristic of the Calcic Chernozem of the forest park.

The appearance of weak ledges at 1650 (Ad) and 1530 cm^{-1} was observed due to the presence of nitrogen-containing groups (amide I and amide II). The intensity of the absorption bands of CH paraffin chains is slightly higher than in the previous profile, but their proportion in the structure of HA is small; the absorption band of benzenoid structures C = C is also clearly expressed at 1605–1620 cm^{-1} .

IR spectra of HA obtained from Ekranic Technosol Urbic Molic U horizon and from the buried horizon (Abur) have no significant distinguishing features in appearance and set of absorption bands when compared to the HA extracted from previous horizons, and are almost identical to each other. They are characterized by a clear absorption band of carboxyl groups (1710 cm^{-1} , 1235 and 1245 cm^{-1} , 2550 cm^{-1}) and a weak shoulder at 1660–1665 cm^{-1} (C = O of quinones). C = C bands of the benzenoid structures are also expressed in the same degree regardless of the depth of sampling. The absorption band of CH groups of paraffin chains is slightly increased in the UR horizon. In the HA preparation from the Abur horizon the bands of mineral components (silicates), characterized by at wavelengths 1035 cm^{-1} , 915 cm^{-1} (shoulder), 525 and 465 cm^{-1} appear more intensive. No noticeable manifestation of nitrogen-containing groups in the form of independent highs can be observed, and the absorption band of OH groups (of different kinds) at 3375–3390 cm^{-1} is due to the strong hydrogen bonds, whereby the long-wave wing turns into a plateau.

4 Discussion

4.1 Humus State of Urban Soils

The most of Calcic Chernozem profiles with a high content of organic matter in the surface horizon is confined to the so-called forest park “protective” belt has framing the city of Rostov-on-Don from its eastern and north-eastern sides. This is due to the fact that under the tree vegetation the way in which the plant residues enter the soil is different from the same process in steppe; as a consequence, there is a change in the distribution of humus along the profile. The presence of litter that is produced in forest from fallen leaves and a thick grass cover, protected from the summer fading by the crowns of the trees, is a source of energetic material, enriching the soil with humus and other mineral and organic compounds. As a consequence, humus profile acquires the features of the forest soil: a quite dramatic humus decrease with depth compared to the upper horizons can be noted. Such pattern of humus distribution is characteristic of the nearest northern “neighbor” of Chernozems – dark gray forest soils (Phaeozems). Ponomareva and Plotnikova [27] called a similar distribution of humus in the soil profile “forest type of accumulation of organic matter”.

Such an increase in the concentration of organic matter in soils of Moscow was mentioned in the works of Prokofieva and others [31], confirming the fact that similar processes are not unique to urban soil of southern Russia.

Thus, the forest-park “protective” plantings at the outskirts of the city ensuring the creation of wind barrier, and thus the favorable climate of the city are also a dynamic environment-forming factor, leading to the formation of “islands” of a totally different type of matter redistribution in the plant-soil system on a background of steppe nutrient

cycle. The tree plantations in steppe are the centers of more intense cycle of matter than the natural steppe communities, and even more intense when compared to arable land.

At the same time, on the fallow plots compared to the cropland some increase in humus content of the upper soil horizons has been noted. When plowing destroys the natural vegetation, the annual flow of all biomass created during the vegetation period stops, and there is a change of redox regime. As a result of this the organic matter changes qualitatively.

Regarding anthropogenically transformed soils, the processes of burial and sealing practically cease the flow of the fresh organic matter to the soil, contemporary processes of humification are damped and, as a consequence, there is no update of humic substances [10]. As a consequence, there is a significant change in the carbon and nitrogen cycles dynamics in the buried soil stratum [17, 26]. In addition, a large proportion of contaminated sediments bypasses soil body, and all this leads to the fact that the possibilities for the soil and humus to conduct their protective features are sharply reduced. Such sealed soils can be regarded as anthropogenic models, reflecting the effect of time on the functioning and the status of soil humic substances system.

Buried soil, unlike sealed under the asphalt (Ekranic Technosol), and does not completely lose contact with the ground surface. Although they lack the influence of many factors of soil formation, they still don't lose their protective function due to partial permeability of the upper strata.

In our study of urban sealed and buried soils significant changes in the content and composition of humus have been found, which is associated with changes in soil conditions and is manifested primarily in the restructuring of the soil profile. Reduction of humus content in Ekranic Technosol and Urbic Technosol Molic is quite clear: the link between soil and plants is disrupted. As a result, the cycling of matter inherent to the steppe zone ceases or changes dramatically.

4.2 The Elemental Composition of Humic Acids

Enrichment of humic acids from park and recreational area Chernozem Ad horizon with nitrogen and hydrogen indicate the relative immaturity of these acids, and significant involvement of peripheral fragments in the structure of their molecules. This fact is explained by the constant updating of humus due to the fresh organic matter entering the soil from the litter of woody plants.

In the arable soil and in buried horizons their amount of fresh organic material is lower. As a result, the mass percent of nitrogen is in the adjacent ranges within both soil types. The exception is urbic horizon, where the mass percent of nitrogen is 4.2%, which may be at part indicative of its anthropogenic origin.

The expression of the elemental composition in mass percentages does not give a complete picture neither of the role of any individual element in the structure of the substance, nor about the changes that occur with humic substances in the soil [22]. Conversion to atomic percentages reveals division between gray and brown humic acids, confirmed by calculations of the oxidation degree, and the analysis of atomic ratios diagram by Van Kleveren method gives the understanding of the direction of the humification process [20].

Increased carbon content in the B1 horizon of the studied soils indicates a specificity of molecular structures at these depths, or rather the dominance of an aromatic central part in their structure. This can be judged more exactly by the ratio (H:C) Rev. (Table 4).

It's common known that the decrease of the H:C ratio indicates an increase in the proportion of aromatic moieties in the molecules of humic acids. But this index is not completely true due to the effect of unaccounted oxygen atoms in the molecule of humic acid, so it is more correct to use the ratio (H:C). Rev., calculated on the basis of the oxygen function in the manner proposed by DS Orlov [22]. The (H:C). Rev. value is calculated as follows:

(H:C). Rev. = (H:C) + 2 * (O:C) * 0,67 where (H:C) is the value found through elemental analysis, 2 is the quotient showing that one oxygen atom can substitute 2 hydrogen atoms, i.e. in a carbonyl group, and 0,67 is a quotient taking into account the presence of different oxygen containing groups, including those that substitute only one hydrogen atom, i.e. hydroxylic groups.

Result of elemental analysis and the ratio (H:C) Rev. have shown that the transformation of humic acids depend on the type of anthropogenic impact. The results show a decline of the ratio (H:C) Rev. in the B1 horizon of all studied soils. In other words, whatever changes is the soil exposed to, the accumulation of more benzenoid HA molecules is always marked at the level of carbonate barrier. The most developed aliphatic part of the HA molecules is found in sod horizon, which is clearly due to constant supply of fresh plant residues and thus "immaturity" of the carbon skeleton of the newly formed HA, containing a higher proportion of hydrogen, nitrogen and sulfur. For the same reasons humic acids obtained from Chernozem of the recreational area of the city stand out for the degree of enrichment with nitrogen.

This is consistent with the chemical analyzes of soil, according to which the ratio of gross amounts of C:N is characterized by a somewhat smaller values.

The tendency to the reduction of the nitrogen content with depth, both in chernozem of the recreational part of the city, and in sealed soils is due to the fact that in the upper horizons the plant residues supply (or supplied, as in the case of sealed profiles) much more nitrogen than the lower layers, and in the process of humification this nitrogen is "captured" by humic acids.

The increased oxidation degree, and the positive $\text{G}\ddot{\text{O}}$ index can serve as an evidence of the most favorable conditions of humification at these depths and leaching of carbonates get some contributes to this process (3). The mentioned data is confirmed by graphical statistical analysis by Van Krevelen method (Fig. 3).

The analysis has shown that the most significant differences are observed in the surface layer of soil. Comparing the Ap, Ad and Abur horizons has shown that woody vegetation is accompanied by a process of methylation of humic acids, which results in the predominance of the peripheral part of the HA.

Sealing the soil leads to the development of oxidation and hydrogenation: the point 2 on the chart (Abur) shifts along the HA molecule hydration line.

The latter is even more characteristic for the plow horizon of the soil of agricultural lands surrounding the city. Humic acids extracted from subsurface horizons A and B1 of the studied soils, are different from each other to a much lesser extent, and this also applies to the buried profile of Chernozem.

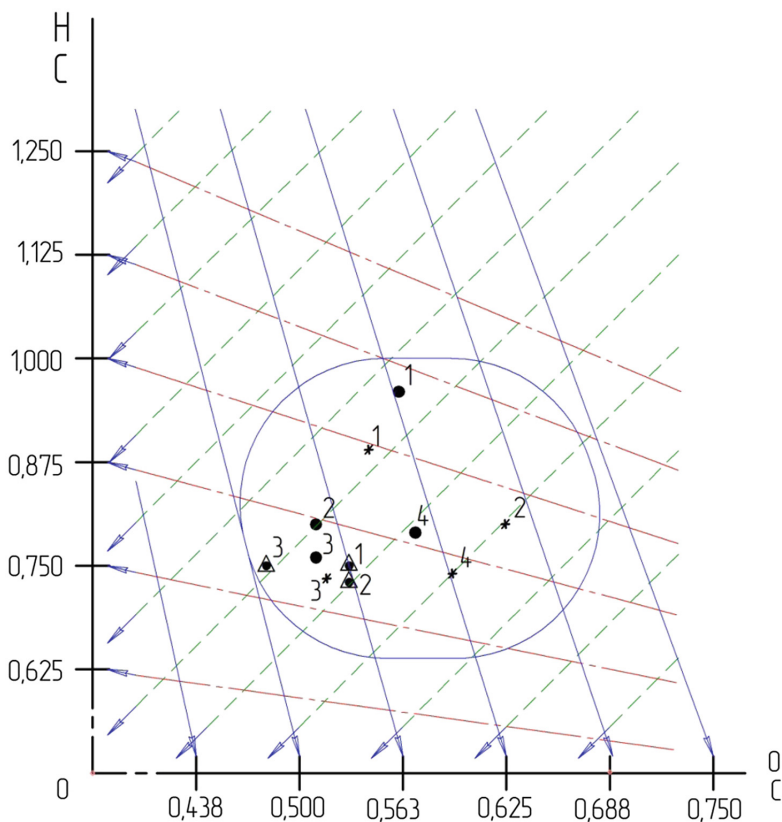


Fig. 3. An analysis of the elemental composition of humic acids by Van Krevelen method:

Δ - Calcic Chernozem Aric (arable land on the outskirts of the city):

1 - Ap horizon; 2 - Ap1 horizon; 3 - B1 horizon;

• - Calcic Chernozem (park and recreational area of the city):

1 - Ad horizon; 2 - A horizon; 3 - B1 horizon; 4 - B2 horizon;

* - Ekranic Technosol, (city center):

1 - UR horizon; 2 - Abur horizon; 3 - B1 horizon; 4 - B2 horizon;



- The direction of demethylation;



- The direction of dehydration;



- The direction of decarboxylation.

4.3 The Optical Density of HA

Electronic absorption spectra and extinction coefficients have become widely used to study the nature of humic substances and they are their diagnostic sign [6]. According to modern concepts the color of humic acids and thus the nature of their electronic spectra are caused by a developed system of conjugated double bonds: these are

multiple carbon-carbon (ethenyl) and carbon-oxygen (carbonyl) communications that are part of the so-called chromophore compounds.

The land use has left its mark on the properties of structural condition of humic acid. The most significant changes have been noted for the HA molecules of the chernozem of the forested area. Along with the lowest values of optical densities in the upper horizons, lower values of this indicator were found throughout the soil profile. Plant residues which are not typical (in their composition) for the steppe area and the migration of newly formed humic substances down the profile lead to the fact that humic acids have less condensed nucleus and thus more developed peripheral portion of the molecule. The lowest level of condensation in the HA molecules from the horizon Ad is due to the presence of newly formed humic acids, which in turn is connected with a constant supply of fresh organic material. This is also evidenced by the results of the functional groups determination – in this horizon of soil under woody vegetation the highest content of hydroxylic and carboxylic groups was found, indicating greater reactivity of humic acids and their relative immaturity.

The UR horizon of the Ekranic Technosol also has lower optical density and high E4:E6 ratio value, close to that of Ad horizon. But taking into account the low quantity of hydroxylic and carboxylic groups in the structure of HA this is rather the evidence of the anthropogenic origin of the horizon. Down the soil profile the optical density of the HA decreases and the chrominance coefficient, respectively, increases.

Thus, the more thermodynamically stable humic acids correspond to higher optical density, lower values of the chrominance coefficient and fewer functional groups.

In his works Salfeld [33] recommends to determine the three extinction coefficients - E400/E500, E500/E600, E600/E700. The spectrum is represented as a point in a three-dimensional coordinate system that allows getting general information about the correlation of the spectra in the system of humic substances of different origin. After these measurements, we found out that, no matter how strong would be the changes in the HA structure of the investigated soils, they still follow the path of transformation, that is typical for the chernozems. This is clearly shown in the Fig. 4.

4.4 The IR Spectra of Humic Acids

All studied humic acids are characterized by high intensity of the absorption bands of carboxyl groups, the benzenoid structures at 1610–1620 cm^{-1} are also clearly manifested.

The increase in the proportion of OH groups (alcohols, possibly phenols), CH groups of the paraffin chains and nitrogen-containing groups (HA of the recreational area of the city chernozems stand out for their nitrogen richness) indicates a higher enrichment of these HA with peripheral aliphatic chains. This is consistent with the data of elemental analysis of humic acids, presented earlier in this article, and is connected, in our opinion, to the characteristics of the fresh organic matter inflow and transformation.

Humic acids extracted from Ekranic Technosol horizons, are very close in their IR spectra to HA of the arable chernozem only to mention a few less intense absorption bands linked to the COOH groups.

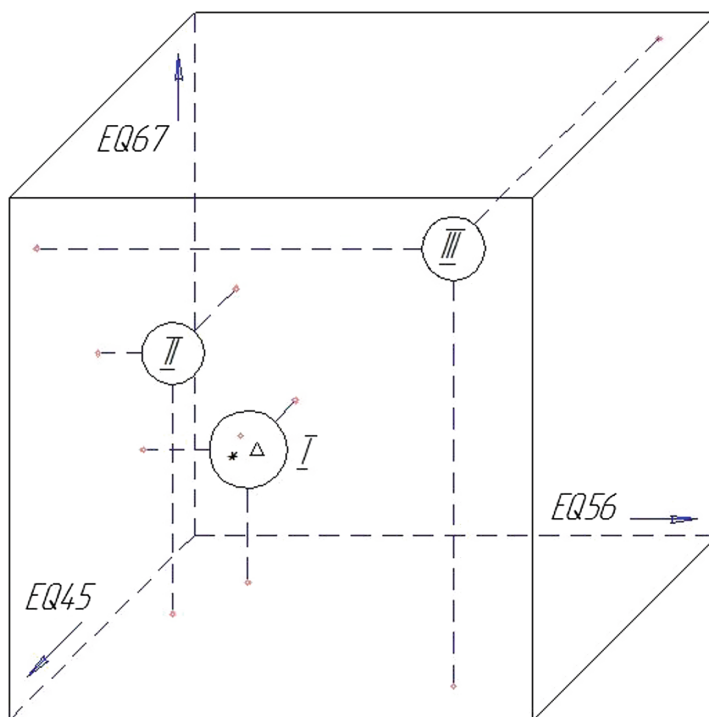


Fig. 4. Schematic model of the imaging the optical density of humic acids using three extinction coefficients.: I – Humic acids of chernozems (\bullet , Δ) and anthropogenically transformed soil of the city (*); II – Humic acids of podzolic soils (from Zalfeld); III – Humic acids of other soil types (from Salfeld, [33]);

5 Conclusions

In the Ekranic Technosol and Urbic Technosol Molic, a significant transformation in the humus content has been found associated with changes in pedogenic conditions and is manifested primarily in the restructuring of the soil profile. Reduction of humus content is a characteristic feature of these soils, since the link between soil and plants is broken. As a result, the matter cycling typical for the steppe zone ceases or changes dramatically.

In soils of the forest-park area of the city, an increase of humus content in the upper 10-cm layer to the average value of $7.5 \pm 0.63\%$ is observed, which significantly exceeds the values of humus content of arable chernozem in the agricultural lands surrounding the city (3.5–4%). The humus profile acquires the features of the forest soil, and as a consequence, a quite dramatic decrease of humus content with depth has been observed.

Specific traits of humus formation in chernozems associated with different kinds of changes in their natural cycle of matter, was reflected in the elemental composition of humic acids. However, in general, humic acids are very stable system, and even under a

very strong anthropogenic impact the changes are not so significant. The changes in the structure of the HA from the studied soils goes on the way that is typical for chernozems.

The most significant changes are noted for HA molecules from the chernozem of the forest park. The plant residues that is not typical for the steppe zone in the quantity and composition lead to the fact that humic acids of these soils are characterized by a smaller aromatic portion of the molecule, and consequently, a more developed peripheral part. The transformation of plant residues is accompanied by a process of methylation of humic acids. Sealing of the soil leads to the development of oxidation and hydrogenation processes. The optical density of the HA from the studied soils is within the limits inherent to the chernozem zone. The most significant changes are noted for HA molecules from the soils of forested area. All HA preparations are characterized by high intensity of the absorption bands of carboxyl groups and a clear manifestation of the benzenoid structures bands at $1610\text{--}1620\text{ cm}^{-1}$. HA of the forest park chernozem are characterized by an increased proportion of the OH groups (alcohols, possibly phenols), CH groups of the paraffin chains and nitrogen-containing groups, which may indicate a higher enrichment of HA with peripheral aliphatic chains. Humic acids extracted from Ekranic Technosol soil horizons are very close in their IR spectra to HA of the arable chernozem only to mention a few less intense absorption bands linked to the COOH groups.

Acknowledgments. This research was supported by project of Ministry Education and Science of Russia, no. 6.6222.2017/BP. Analytical work was carried out on the equipment of Centers for Collective Use of Southern Federal University “Biotechnology, Biomedical and Environmental Monitoring” and “High Technology”.

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