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Article

Ecological and geochemical state of natural and anthropogenically transformed soils of residential areas in Rostov-on-Don

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Abstract. This paper assesses heavy metal pollution in soils of residential areas in Rostov-on-Don. The objects of the study were soils of natural origin – migration-segregation thick medium-humus heavy loamy chernozems on loess-like loams and anthropogenically transformed soils – urbostratified chernozems and urban stratozems on buried migration-segregation chernozems on loess-like loams. Comparative analysis with the background analog showed a low level of chernozems contamination by heavy metals ($Z_c = 4.5–6.0$). The greatest accumulation of pollutants was observed in bulk and anthropogenic transformed horizons. The maximum values of K_c were recorded in the urbic horizons for cobalt ($K_c = 1.6–2.6$), copper ($K_c = 1.2–3.7$), zinc ($K_c = 1.6–6.7$) and lead ($K_c = 1.5–6.1$). In general, there is a clear tendency towards decreasing levels of contamination of the underlying horizons by these elements, which indicates the barrier properties exhibited by urbanozems due to the increased density of urban horizons. The primary pollutants of anthropogenically transformed soils are zinc and arsenic. Their concentrations do not exceed two APC. According to sanitary and hygienic standards, this type of soil is considered to have an acceptable level of pollution ($Z_c < 16$). Under the impact of anthropogenic load, localized contaminations with copper in mobile form (16.6 MPC) as well as lead (5.3 APC) were recorded in the uppermost horizons. Despite an excess of APC for pollutants in transformed soils of residential areas, the presence of urban horizons characterized by increased density, and carbonate barriers in buried chernozems slows down the migration of metals deep into the profile, thereby mitigating the anthropogenic load on black soil.

Keywords: migration-segregation chernozems, urban stratozems, urban stratified chernozems, heavy metals

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Научная статья

Эколого-геохимическое состояние естественных и антропогенно- преобразованных почв селитебных территорий г. Ростов-на-Дону

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Аннотация. Приводятся данные по оценке загрязнения тяжелыми металлами почв селитебных зон г. Ростов-на-Дону. Объектами исследования выступали почвы естественного происхождения – черноземы миграционно-сегрегационные мощные среднегумусированные тяжелосуглинистые на лессовидных суглинках и антропогенно-преобразованные почвы – урбостратифицированные черноземы и урбостратоземы на погребенных черноземах миграционно-сегрегационных на лессовидных суглинках. Сравнительный анализ с фоновым аналогом показал низкую степень загрязнения черноземов тяжелыми металлами ($Z_c = 4.5–6.0$). Наибольшее скопление поллютантов можно наблюдать в насыпных и антропогенно-преобразованных горизонтах. Максимальные значения K_c зарегистрированы в горизонтах «урбик» для кобальта ($K_c = 1.6–2.6$), меди ($K_c = 1.2–3.7$), цинка ($K_c = 1.6–6.7$) и свинца ($K_c = 1.5–6.1$). В целом прослеживается явная тенденция к снижению интенсивности загрязнения элементами нижележащих горизонтов, что свидетельствует о барьерных свойствах, проявляемых урбаноземами, за счет повышенной плотности урбиковых

горизонтов. Основными поллютантами антропогенно-преобразованных почв выступают цинк и мышьяк, их содержание не превышает 2 ОДК, с учетом санитарно-гигиенических критериев данный тип почв характеризуется допустимым уровнем загрязнения ($Z_c < 16$). Под влиянием техногенной нагрузки в дневных горизонтах отмечены локальные очаги загрязнения медью в подвижной форме (16.6 ПДК), а также свинцом (5.3 ОДК). Несмотря на превышение ОДК поллютантов в трансформированных почвах селитебных зон, наличие урбогоризонтов, для которых характерна повышенная плотность, и карбонатных барьеров в погребенных черноземах замедляет миграцию металлов вглубь профиля, смягчая антропогенную нагрузку на черноземы.

Ключевые слова: миграционно-сегрегационные черноземы, урбостратоземы, урбостратифицированные черноземы, тяжелые металлы

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Introduction

Soil degradation under anthropogenic stress is one of the pressing issue of soil science and ecology (Danila and Saulius, 2017; Zhang et al., 2020). The increasing industrial potential of megacities inevitably leads to the involvement of chemical substances in a number of anthropogenic transformations and, as a consequence, their negative impact on all parts of the ecosystem, including human health (Arkhipova et al., 2014; Sarwar et al., 2017).

Soil contamination with heavy metals is the most hazardous category of pollution that can affect the entire biocenosis (Li et al., 2019; Tchounwo et al., 2012). Pollution of the surface soil layer with heavy metals is considered in close interaction with the adjacent air environment. It is usually associated with atmospheric transport of motor vehicle exhaust gases as well as emissions from industrial plants. In addition, the creation of landfills and the burial of human waste make a significant contribution to the process of soil pollution.

In order to accurately assess the ecological state of soil, it is essential to consider the specific chemical form of metals present in it, since it is bioavailability of the elements that determines their toxic effect. Once in the soil, metals become mobile due to chelation processes with humic and fulvic acids, or are sorbed by minerals and retained in both exchangeable and non-exchangeable forms (Bauer et al., 2022; Kloster and Marcelo, 2015; Minkina, et al., 2018; Pinskiy and Minkina, 2013; Vodyanitsky, 2005). Subsequently, the mobile forms of heavy metals are included in the biogeochemical cycle, being absorbed by plants, which accumulate them in vegetative organs. Excessive metal concentrations in plant tissues can lead not only to disruption of plant homeostasis mechanisms, but also to the subsequent transfer of these elements through trophic levels into the human body, eventually adversely affecting its health (Bashkin et al., 1993; Gu et al., 2016).

However, certain soil parameters, in particular the pH of the soil solution, may impede the transition of metals into a mobile form. It is worth noting that phytocenoses have mechanisms to prevent excessive accumulation and translocation of metals into the aboveground portion of plants (Gonzalez Henao and Ghneim-Herrera, 2021; Verma et al, 2021; Wang et al., 2021). Studies on metal translocation in the "soil-plant" system show that plants primarily establish physiological barriers through the selective absorption and subsequent accumulation of elements in their root system, as well as the isolation of metals in metallothioneins (Chernaska, 1989; Petukhov et al., 2022).

Understanding the mechanisms of heavy metal migration in different soils provides invaluable geoecological information regarding their distribution profiles and the potential for groundwater contamination, which is especially important in urban landscapes (Evstafieva et al., 2018; Issaka and Ashraf, 2017; Zharikova, 2021). The problem of geochemical pollution is most acute in large cities, where population growth is accompanied by an increase in the proportion of industrial enterprises. In Rostov-on-Don, for instance, such enterprises include a number of companies: Empils paint and varnish company, Large-Panel Housebuilding Plant, Baltika and Solnechny breweries.

Our work aimed to assess the geochemical state of natural and anthropogenically altered soils of residential areas in Rostov-on-Don.

Materials and methods

As one of the most densely populated cities in southern Russia, Rostov-on-Don has undergone significant changes in the localization of industrial enterprises. In order to reduce the technogenic load on the residential areas of the city, most of the enterprises were relocated to the left bank of the Don River, thus creating a barrier between industrial and residential areas. Monitoring studies of the biogeochemical state of soils in Rostov-on-Don were conducted during different time periods with reference to the functional zones in the city (Bezuglova et al., 2019b; Dubinina et al., 2016; Gorbov et al., 2015a, b; Sobornikova and Kizilshtein, 1990;). In their work, based on complex diagnostics, S.N. Gorbov et al. (2015b) proved the absence of correlation between the genotoxicity indicators of different types of soil and the content of heavy metals.

Due to the land use practices, urban stratozems consisting of anthropogenic horizons formed on buried chernozems have developed in the city. However, in different districts of the city, it is still possible to find native soils that have retained their original appearance – migration-segregation chernozems. In the process of urban pedogenesis, soils in the city develop certain features related to the transformation of their morphological, physical and chemical properties. It was observed that in urbostratozems and urban stratified chernozems, the thickness of the humus-accumulative layer, as well as the depth of occurrence of white-eyed deposits, decreases in comparison with migratory-segregation chernozems (Tagiverdiev et al., 2021). The region is characterized by a temperate continental climate with rather hot and dry summers, which significantly affects the migration of carbonates in the soil profile. This causes the formation of zones of large salt accumulations and affects the distribution of metals in a certain way (Bezuglova et al., 2019a; Minaeva et al., 2021).

This study is focused on soils of natural origin – migration-segregation thick medium-humus heavy loamy chernozems on loess-like loams (boreholes P20-35, P21-42) and anthropogenically transformed soils – urbostratified chernozems and urban stratozems on buried migration-segregation chernozems on loess-like loams (boreholes P20-28, P20-37, P21-39, P21-40, P21-43, P21-44, P21-46, P21-49, P20-24-1), as well as replanted urban stratozems (boreholes P20-36, P20-38) (Table. 1). The boreholes were drilled in functional residential and transportation zones encompassing the most industrially active districts of the city: Sovetsky, Zheleznodorozhny, Oktyabrsky, Proletarsky, Voroshilovsky, and Leninsky (Fig. 1).

To assess the potential for heavy metal migration to underlying layers, soil samples were collected from all genetic and anthropogenic horizons.

The elemental composition of soils was determined with the Spectroscan MAKS-GVM instrument (Russia) using the X-ray fluorescence method. The MGA-915 atomic absorption spectrophotometer (Russia) was utilized to measure the concentration of mobile metals in soils. The extraction of mobile metal forms was performed using an ammonium acetate buffer solution (pH 4.8) at a soil-to-extractant ratio of 1:10.

Table 1. Geographic coordinates of sampling locations and main characteristics of soils in Rostov-on-Don.

Borehole number/ coordinates	Soil type in accordance with WRB (2014) and "Classification and diagnostics of soils in Russia" (Shishlov et al., 2004)	Depth, cm	C _{org} ^r % (Sleutel et al., 2007)	pH _{wat}
P17-01/ N 47°14'03.24" E 39°39'25.87"	Calcic Chernozems	0–10	3.12	8.0
		10–50	1.89	8.4
		50–70	1.32	8.5
		70–95	0.93	8.6
		95–120	0.86	8.6
		120–150	0.53	8.7
P20-24-1/ N 47°15'19.50" E 39°42'38.60"	Urbic Technosols	0–10	2.68	6.9
		10–20	2.51	7.3
		20–30	1.93	7.1
		30–50	1.14	7.3
P20-28/ N 47°13'54.64" E 39°44'55.85"	Urbic Technosols	0–10	3.85	7.1
		10–20	1.61	7.1
		20–30	2.20	7.2
		30–50	0.83	6.8
P20-35/ N 47°11'59.57" E 39°37'13.93"	Calcic Chernozems	0–10	1.84	7.1
		10–20	1.66	7.8
		20–30	1.51	7.1
		30–50	1.28	7.8
		50–70	0.69	7.7
		70–90	0.57	8.0
		90–100	2.40	7.7

Borehole number/ coordinates	Soil type in accordance with WRB (2014) and "Classification and diagnostics of soils in Russia" (Shishlov et al., 2004)	Depth, cm	C _{орг} , % (Sleutel et al., 2007)	pH _{wat}
P20-36/ N 47°13'50.34" E 39°37'4.29"	Urbic Technosols Урбостратозем реплантированный тяжелосуглинистый	0–15	1.26	7.8
		15–30	3.11	8.0
P20-37/ N 47°14'9.26" E 39°38'3.59"	Urbic Technosols Урбостратозем среднесуглинистый на черноземе миграционно-сегрегационном среднемощном среднегумусированном тяжелосуглинистом	0–10	2.76	8.0
		10–20	1.99	7.5
		20–30	2.01	7.9
		30–40	2.05	7.9
		40–50	1.74	7.7
		50–70	1.41	7.9
		70–90	0.94	7.9
		90–100	0.66	8.0
		100–110	2.90	8.1
		P20-38/ N 47°13'35.60" E 39°37'54.66"	Urbic Technosols Урбостратозем реплантированный тяжелосуглинистый	0–10
10–20	1.70			7.8
20–30	0.75			7.9
30–50	1.04			7.7
P21-39/ N 47°12'54.66" E 39°40'28.87"	Urbic Technosols Урбостратозем на погребенном черноземе миграционно-сегрегационном тяжелосуглинистом	0–20	2.76	8.0
		20–50	1.71	8.5
		50–70	1.18	9.1
		70–90	0.98	8.6
		90–100	0.79	8.5
P21-40/ N 47°13'26.45" E 39°42'13.42"	Urbic Technosols Урбостратозем на погребенном черноземе миграционно-сегрегационном среднесуглинистом	100–120	0.14	7.4
		0–25	1.64	7.8
		25–50	1.90	8.4
		50–70	0.38	8.2
		70–80	1.41	7.5
	80–110	0.83	7.8	

Borehole number/ coordinates	Soil type in accordance with WRB (2014) and "Classification and diagnostics of soils in Russia" (Shishlov et al., 2004)	Depth, cm	C _{org} % (Sleutel et al., 2007)	pH _{wat}
P21-42/ N 47°14'18.45" E 39°48'38.29"	Calcic Chernozems Чернозем миграционно-сегрегационный тяжелосуглинистый	0–20	1.40	7.5
		20–50	1.41	7.8
		50–60	1.45	7.5
		60–75	0.3	7.8
		75–90	0.45	8.3
		90–120	0.29	8.1
P21-43/ N 47°14'8.29" E 39°49'44.96"	Urbic Technosols Урбистратифицированный чернозем миграционно-сегрегационный среднесуглинистый	0–10	3.14	7.5
		10–20	2.22	7.6
		20–40	1.77	7.3
		40–60	1.44	7.3
		60–80	1.32	7.8
		80–100	0.58	7.5
P21-44/ N 47°14'30.08" E 39°50'19.38"	Urbic Technosols Урбостратозем на погребенном черноземе миграционно-сегрегационном среднесуглинистом	100–120	0.6	8.3
		0–10	1.74	7.9
		10–30	0.55	7.9
		30–50	0.92	7.6
		50–70	1.35	7.9
P21-46/ N 47°12'26.56" E 39°38'25.16"	Urbic Technosols Урбистратифицированный чернозем миграционно-сегрегационный среднесуглинистом	70–90	1.11	7.8
		90–120	0.92	8.9
		0–20	1.9	7.7
		20–40	1.05	9.2
		40–65	1.08	7.9
P21-49/ N 47°15'42.76" E 39°40'3.78"	Urbic Technosols Урбостратозем на погребенном черноземе миграционно-сегрегационном тяжелосуглинистом	65–90	0.71	8.0
		90–120	0.19	7.9
		0–20	1.98	8.0
		20–50	0.46	7.8
		50–60	2.55	7.7
		60–90	3.58	7.7
		90–100	0.94	7.9

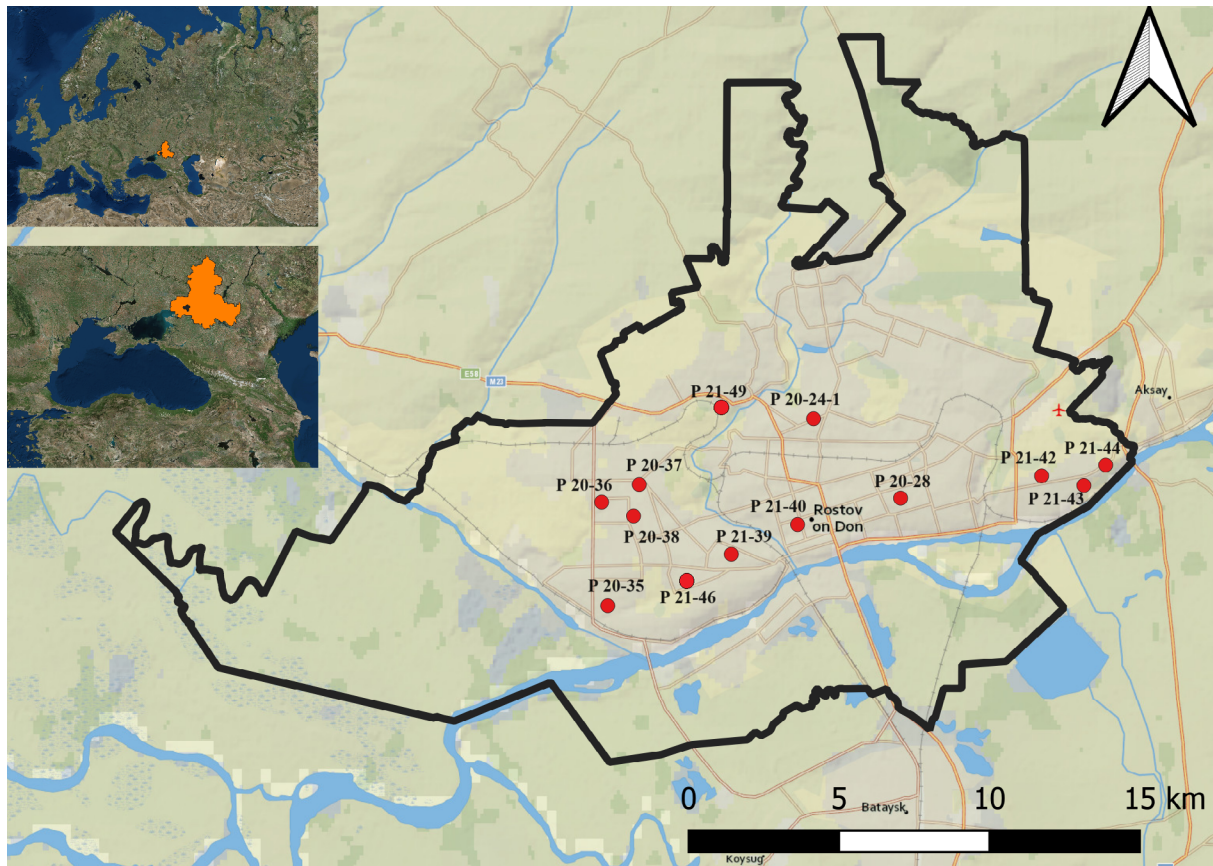


Fig. 1. Map of sampling locations in Rostov-on-Don. Red dots indicate boreholes of anthropogenically transformed soils and green dots indicate native soil of the background section.

The following coefficients were calculated to assess the degree of contamination:

hazard coefficient

$$K_h = \frac{C_i}{MPC},$$

technogenic concentration coefficient

$$K_c = \frac{C_i}{C_{bi}},$$

total pollution index

$$Z_c = \sum K_{Ci} - (n-1),$$

where: C_i – concentration of an element, C_{bi} – background concentration of the same element, n – number of pollutants.

The 1950s data on the content of elements in migration-segregation chernozems (Akimtsev et al., 1962) were used as the background concentration. For comparison we used conditional background concentrations of metals measured in the soil section P17-01, located in the Botanical Garden of the Southern Federal University (SFU).

To reveal patterns of elements accumulation or removal in migration-segregation chernozems, the removal/accumulation coefficients (EA) were calculated as the ratio of metal concentration in the horizon under study to its content in the rock.

Mathematical data processing was carried out using generally accepted methods of variation statistics, with Microsoft Excel 2016 and Statistica 13.0 software package.

Results

To assess the degree of pollution of natural soils in the residential area of the city, the content of metals in gross form was compared with the background values obtained for the soil from the SFU Botanical Garden (Table 2). The analysis was conducted for the surface layer (0–10 cm), since it is in this layer that changes in the degree of soil contamination and potential environmental risks are most pronounced. The Z_c value for background was found to be higher than that for the city soils. This phenomenon can be explained by the entry of coarse and medium sand fractions to a depth of 0–10 cm, for example, with de-icing agents, which can lead to a decrease in total metal content. In an earlier study, the authors showed that urban pedogenesis processes in all the soils under study in Rostov agglomeration resulted in an increase in the proportion of sand fractions in the surface and middle horizons of chernozems (Bezuglova et al., 2018). On the other hand, the elevated levels of trace elements in the surface layer of the background soil compared to the city soils may be caused by the intake of metals from leaf litter, in which they accumulate during the vegetation process.

The greatest accumulation of pollutants can be observed in bulk and anthropogenically transformed horizons (Tables 3, 4). The maximum K_n values were recorded in the urbic horizons for cobalt ($K_c = 1.6$ – 2.6), copper ($K_c = 1.2$ – 3.7), zinc ($K_c = 1.6$ – 6.7) and lead ($K_c = 1.5$ – 6.1). However, concentrations of individual elements can vary considerably between different horizons and boreholes. In general, there is a clear tendency towards a decrease in the intensity of pollution by elements of the underlying horizons, which indicates the buffer capacity of urban soils. Our assessment of the removal or accumulation of elements, based on the ratio of their concentrations in the genetic horizon to that in the rock, showed accumulation of zinc and lead in the surface soil layer of the residential area, which is a consequence of technogenic impacts (Table 5). In particular, this is especially evident in borehole P20-35, where EA values significantly decrease as you go down the profile. In general, most elements in the surface horizons show moderate accumulation rates ($EA = 1.1$ – 1.4).

In both qualitative and quantitative terms, the accumulation and distribution of elements in the genetic horizons of borehole P21-42 are largely comparable with the background values, and the obtained Z_c (Table 2) and EA (Table 5) values indicate permissible levels of heavy metal pollution in this area (in accordance with SanPiN 1.2.3685-21¹) and their moderate accumulation. Thus, the observed patterns of accumulation and distribution of trace elements in the soil column of migration-segregation chernozems make it clear that proximity to pollution sources has a significant impact on natural soils in the city.

Z_c values for both urban stratozems and urban stratified chernozems are greater than one and vary over a fairly wide range, even within one district, from 3.3 (Aleksandrovka microdistrict, Proletarsky district, borehole P21-44) to 16.8 (Nakhichevan microdistrict, Proletarsky district, borehole P20-28), which is obviously explained by different remoteness of these territories from the source of anthropogenic pollution (Table 3). In the latter case, the level of pollution at a depth of 0-10 cm is considered moderately hazardous, with zinc and lead making the greatest contribution to pollution. According to the hazard scale, pollution levels in Sovetsky ($Z_c = 7.2$ – 8.2), Oktyabrsky ($Z_c = 6.1$), Zheleznodorozhny ($Z_c = 8.4$), Proletarsky ($Z_c = 3.3$ – 16.8), and Leninsky ($Z_c = 7.9$ – 8.1) districts are within the permissible range. Thus, soils in residential zones of the city are characterized by insignificant pollution levels of metals. The elements are distributed relatively evenly throughout the profile, including the parent rock. Their concentrations do not exceed the APC, except for zinc, arsenic, and chromium.

Discussion

Analysis of the gross forms of metals revealed the excess of zinc relative to the APC values (Table 4) in the surface horizons of urban stratozems and urban stratified chernozems in boreholes P20-28 (2 APC), P20-37 (1.4 APC), P21-40 (1.4 APC), and P21-46 (1.1 APC). The elevated zinc concentrations are associated with the uptake of this metal of aerogenic origin by the soil. Since 1926, a chemical plant for the production of zinc whitewash (now JSC "Empils") has operated in the city. This plant was the main source of zinc contamination in the topsoil. The plant was later relocated to the northwestern industrial zone, but the production facility remaining in the central part of the city is still in operation. Nevertheless,

¹ SanPiN 1.2.3685-21 Hygienic standards and requirements for ensuring the safety and (or) harmlessness of environmental factors for humans.

Table 2. Concentration coefficients of gross forms of metals (K_g) and total pollution indices (Z_c) of migration-segregation chernozems.

Depth, cm	Element											Z_c
	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb		
Calcic Chernozems of the SFU Botanical Garden P17-01												
0–10	1.75	1.59	1.60	1.51	1.29	1.78	3.83	1.59	0.47	1.83		8.77
10–50	1.98	1.33	1.64	1.89	1.27	1.80	2.91	1.22	0.47	1.27		7.31
50–70	1.69	1.25	1.44	2.49	1.28	1.94	2.87	0.63	0.56	0.40		6.94
70–95	1.69	1.05	1.24	2.38	1.09	1.93	2.72	0.98	0.66	0.91		6.11
95–120	1.56	1.39	1.19	2.21	1.01	1.85	2.51	1.01	0.72	0.95		5.73
120–150	1.67	1.12	1.33	2.59	1.08	2.11	2.81	1.15	0.86	1.17		7.03
Calcic Chernozems P21-42												
0–20	1.20	1.34	1.22	2.11	1.00	1.27	1.44	1.44	0.46	0.83		4.02
20–50	1.36	1.24	1.37	2.67	0.96	1.16	0.98	0.86	0.45	1.22		4.01
50–60	1.41	0.94	1.31	2.97	0.94	1.05	0.87	0.77	0.43	1.44		4.17
60–75	1.31	1.15	1.12	2.38	1.04	1.44	0.93	1.12	0.58	1.07		3.62
75–90	1.38	1.08	1.13	2.16	1.03	1.33	0.97	1.20	0.58	0.82		3.31
90–120	1.26	0.98	1.02	2.37	0.89	1.51	0.95	1.44	0.76	1.07		3.67
Calcic Chernozems P20-35												
0–10	1.18	0.91	1.24	2.62	0.77	0.91	2.24	0.76	0.46	3.22		6.49
10–20	1.14	0.97	1.15	1.81	0.79	1.25	2.14	1.17	0.45	2.18		4.84
20–30	1.07	0.96	1.18	1.84	0.79	1.16	1.73	1.15	0.42	2.02		4.15
30–50	1.27	0.91	1.12	2.75	0.82	0.83	1.15	0.73	0.40	1.49		3.78
50–70	1.15	1.02	0.99	2.83	0.79	1.00	0.99	0.83	0.43	1.18		3.19
70–90	1.16	0.73	0.95	2.20	0.70	0.94	0.97	0.83	0.47	1.07		2.43
90–дно	0.90	0.76	0.88	1.96	0.74	0.86	0.95	0.94	0.52	0.97		1.96

Table 3. Concentration coefficients of heavy metals (K_c) and total pollution indices (Z_c) of anthropogenically transformed soils.

Depth, cm	Element											Z_c
	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb		
	Urbic Technosols P20-37 (Sovetsky district)											
0–10	1.26	1.07	1.22	1.64	0.87	1.23	4.89	1.17	0.60	1.68	7.16	
10–20	1.28	1.03	1.23	2.22	0.85	1.26	3.84	0.86	0.57	1.67	6.53	
20–30	1.34	0.93	1.40	1.46	0.93	1.16	3.25	0.80	0.53	1.61	5.23	
30–40	1.27	0.99	1.42	2.03	1.05	1.28	2.45	1.18	0.54	1.25	4.93	
40–50	1.37	1.16	1.70	2.02	1.21	1.10	1.45	0.82	0.52	1.77	4.76	
50–70	1.31	1.24	1.61	2.05	1.19	0.99	1.35	0.48	0.49	1.78	4.53	
70–90	1.52	1.17	1.53	2.01	1.20	1.01	1.25	0.70	0.49	1.93	4.62	
90–100	1.25	1.23	1.49	2.30	1.14	1.07	1.20	0.63	0.52	1.65	4.32	
100–110	1.22	1.02	1.40	2.05	1.10	1.05	1.17	0.96	0.57	1.38	3.40	
	Urbic Technosols P21-39 (Zheleznodorozhny district)											
0–20	1.07	0.95	1.20	2.21	0.90	1.61	3.35	1.51	0.67	3.46	8.42	
20–50	1.39	1.18	1.19	2.11	0.96	1.50	1.80	1.50	0.63	1.49	5.16	
50–70	1.26	1.47	1.20	1.47	1.04	1.27	1.08	1.35	0.57	1.01	3.16	
70–90	1.19	0.87	1.13	2.19	0.97	1.31	0.98	1.10	0.59	1.03	2.94	
90–100	1.48	0.98	1.05	1.95	0.91	1.43	0.92	1.31	0.62	1.18	3.39	
100–120	1.37	1.00	1.05	2.14	0.91	1.34	0.95	0.91	0.68	1.06	2.97	
	Urbic Technosols P21-40 (Leninsky district)											
0–25	0.62	0.73	0.69	2.56	0.50	1.59	4.59	0.55	0.70	2.14	7.87	
25–50	1.29	1.12	1.60	2.68	0.94	1.91	2.19	2.07	0.91	3.70	9.56	
50–70	0.67	0.74	1.26	2.03	0.79	2.20	1.33	2.55	1.00	4.04	8.41	
70–80	1.39	0.98	1.40	2.18	1.00	1.41	1.17	1.28	0.62	2.25	5.09	
80–110	1.54	1.36	1.41	2.42	1.07	1.26	1.06	0.73	0.51	1.74	4.86	
	Urbic Technosols P21-44 (Proletarsky district)											
0–10	0.65	1.06	0.99	1.55	0.67	1.36	1.61	1.24	0.46	1.48	3.30	

Depth, cm	Element											Z _c
	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb	Z _c	
10–30	1.05	0.98	1.12	2.00	0.89	1.51	1.06	0.98	0.59	1.59	3.33	
30–50	1.36	1.52	1.33	2.87	0.92	1.42	1.06	1.18	0.57	1.49	5.22	
50–70	1.34	1.47	1.47	2.31	1.01	1.32	1.28	1.20	0.51	1.34	4.74	
70–90	1.24	1.37	1.42	2.40	0.98	1.44	1.05	1.40	0.48	1.31	4.63	
90–120	1.34	1.01	1.16	2.69	1.01	1.49	0.98	1.04	0.52	1.07	3.82	
Urbic Technosols P21-46 (Sovetsky district)												
0–20	1.13	1.03	1.08	2.02	0.76	1.35	3.65	0.61	0.48	3.90	8.16	
20–40	1.28	1.03	1.39	3.12	0.92	1.51	1.92	1.12	0.56	1.63	6.00	
40–65	1.02	0.98	1.37	2.84	0.94	1.60	1.63	1.08	0.53	1.49	5.03	
65–90	1.19	1.14	1.17	2.73	1.03	1.41	1.45	0.74	0.54	1.36	4.47	
90–120	1.10	1.19	1.05	3.13	0.89	1.51	0.98	1.43	0.59	1.11	4.52	
Urbic Technosols P21-49 (Oktyabrsky district)												
0–20	1.53	1.05	1.67	1.99	1.22	1.50	1.45	1.02	0.56	2.64	6.07	
20–50	0.98	0.91	1.12	1.63	0.77	1.80	1.78	0.69	0.59	2.06	4.39	
50–60	1.12	0.91	1.33	1.74	1.08	2.00	6.21	1.21	0.65	1.76	9.44	
60–90	0.90	0.87	1.18	1.09	1.16	2.16	11.94	1.66	0.65	1.48	14.67	
90–100	1.19	0.99	1.27	1.29	1.11	1.87	2.68	1.71	0.57	1.03	5.16	
Urbic Technosols P20-24-1 (Leninsky district)												
0–10	1.57	1.51	1.87	3.18	1.39	1.68	1.54	0.55	0.54	2.33	8.07	
10–20	1.46	1.05	1.80	1.72	1.29	1.65	2.16	1.36	0.58	1.71	6.18	
20–30	1.39	1.28	1.57	1.35	1.14	2.06	4.09	2.39	0.69	5.53	12.80	
30–50	1.24	1.26	1.34	1.46	1.13	1.82	1.51	1.42	0.66	1.30	4.46	
Urbic Technosols P20-28 (Proletarsky district)												
0–10	0.94	1.21	1.75	1.55	0.97	3.74	6.72	1.81	0.74	6.07	16.84	
10–20	0.82	0.96	1.43	1.32	0.80	3.27	3.43	2.77	1.29	3.46	10.98	
20–30	1.28	0.89	1.33	2.79	0.82	2.77	3.30	1.72	1.04	3.85	11.08	
30–50	0.53	0.73	0.93	1.88	0.57	1.26	1.56	0.65	0.88	1.70	3.40	

Table 4. Hazard coefficient (K_h) values of gross forms of metals in anthropogenically transformed soils.

Depth, cm	Element									
	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb
	Urbic Technosols P20-37									
0–10	0.56	1.07	0.45	0.26	0.49	0.28	1.45	0.94	0.30	0.26
10–20	0.57	1.03	0.45	0.35	0.48	0.29	1.14	0.69	0.28	0.26
20–30	0.60	0.93	0.51	0.23	0.52	0.26	0.96	0.64	0.26	0.25
30–40	0.57	0.99	0.52	0.33	0.59	0.29	0.72	0.95	0.27	0.19
40–50	0.61	1.16	0.62	0.32	0.68	0.25	0.43	0.66	0.26	0.27
50–70	0.59	1.24	0.59	0.33	0.67	0.23	0.40	0.39	0.25	0.27
70–90	0.68	1.17	0.56	0.32	0.67	0.23	0.37	0.56	0.24	0.30
90–100	0.56	1.23	0.55	0.37	0.64	0.24	0.36	0.50	0.26	0.25
100–110	0.55	1.02	0.52	0.33	0.62	0.24	0.35	0.77	0.28	0.21
	Urbic Technosols P21-39									
0–20	0.48	0.95	0.44	0.35	0.51	0.37	0.99	1.21	0.33	0.53
20–50	0.62	1.18	0.44	0.34	0.54	0.34	0.53	1.20	0.32	0.23
50–70	0.56	1.47	0.44	0.24	0.58	0.29	0.32	1.08	0.28	0.16
70–90	0.53	0.87	0.42	0.35	0.55	0.30	0.29	0.88	0.29	0.16
90–100	0.66	0.98	0.38	0.31	0.51	0.32	0.27	1.05	0.31	0.18
100–120	0.61	1.00	0.38	0.34	0.51	0.30	0.28	0.73	0.34	0.16
	Urbic Technosols P21-40									
0–25	0.28	0.73	0.25	0.41	0.28	0.36	1.35	0.44	0.35	0.33
25–50	0.58	1.12	0.59	0.43	0.53	0.43	0.65	1.66	0.46	0.57
50–70	0.30	0.74	0.46	0.32	0.44	0.50	0.39	2.04	0.50	0.62
70–80	0.62	0.98	0.51	0.35	0.56	0.32	0.35	1.03	0.31	0.35
80–110	0.69	1.36	0.52	0.39	0.60	0.29	0.31	0.58	0.26	0.27
	Urbic Technosols P21-44									
0–10	0.29	1.06	0.36	0.25	0.38	0.31	0.47	0.99	0.23	0.23

Depth, cm	Element									
	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb
10–30	0.47	0.98	0.41	0.32	0.50	0.34	0.31	0.78	0.30	0.24
30–50	0.61	1.52	0.49	0.46	0.52	0.32	0.31	0.94	0.29	0.23
50–70	0.60	1.47	0.54	0.37	0.57	0.30	0.38	0.96	0.25	0.21
70–90	0.55	1.37	0.52	0.38	0.55	0.33	0.31	1.12	0.24	0.20
90–120	0.60	1.01	0.43	0.43	0.57	0.34	0.29	0.83	0.26	0.16
Urbic Technosols P21-46										
0–20	0.51	1.03	0.40	0.32	0.43	0.31	1.08	0.49	0.24	0.60
20–40	0.57	1.03	0.51	0.50	0.52	0.34	0.57	0.89	0.28	0.25
40–65	0.46	0.98	0.50	0.45	0.53	0.36	0.48	0.86	0.27	0.23
65–90	0.53	1.14	0.43	0.44	0.58	0.32	0.43	0.59	0.27	0.21
90–120	0.49	1.19	0.39	0.50	0.50	0.34	0.29	1.14	0.30	0.17
Urbic Technosols P21-49										
0–20	0.69	1.05	0.61	0.32	0.69	0.34	0.43	0.81	0.28	0.41
20–50	0.44	0.91	0.41	0.26	0.43	0.41	0.52	0.55	0.29	0.32
50–60	0.50	0.91	0.49	0.28	0.61	0.45	1.83	0.97	0.33	0.27
60–90	0.40	0.87	0.43	0.17	0.65	0.49	3.53	1.33	0.33	0.23
90–100	0.53	0.99	0.47	0.21	0.63	0.42	0.79	1.37	0.29	0.16
Urbic Technosols P20-24-1										
0–10	0.70	1.51	0.69	0.51	0.78	0.38	0.46	0.44	0.27	0.36
10–20	0.65	1.05	0.66	0.28	0.72	0.37	0.64	1.09	0.29	0.26
20–30	0.62	1.28	0.58	0.22	0.64	0.47	1.21	1.91	0.35	0.85
30–50	0.55	1.26	0.49	0.23	0.63	0.41	0.45	1.13	0.33	0.20
Urbic Technosols P20-28										
0–10	0.42	1.21	0.64	0.25	0.54	0.85	1.99	1.44	0.37	0.93
10–20	0.37	0.96	0.52	0.21	0.45	0.74	1.01	2.21	0.65	0.53
20–30	0.57	0.89	0.49	0.45	0.46	0.63	0.97	1.38	0.52	0.59
30–50	0.24	0.73	0.34	0.30	0.32	0.29	0.46	0.52	0.44	0.26

Depth, cm	Element										
	V	Cr	Mn	Co	Ni	Cu	Zn	As	Sr	Pb	
Urbic Technosols P20-37 (Sovetsky district)											
0–10	1.0	1.1	0.9	0.8	0.8	1.2	4.2	1.2	1.1	1.2	
10–20	1.1	1.0	0.9	1.1	0.8	1.2	3.3	0.9	1.0	1.2	
20–30	1.1	0.9	1.0	0.7	0.8	1.1	2.8	0.8	0.9	1.2	
30–40	1.0	1.0	1.0	1.0	1.0	1.2	2.1	1.2	1.0	0.9	
40–50	1.1	1.1	1.2	1.0	1.1	1.0	1.2	0.8	0.9	1.3	
50–70	1.1	1.2	1.1	1.0	1.1	0.9	1.2	0.5	0.9	1.3	
70–90	1.2	1.2	1.1	1.0	1.1	1.0	1.1	0.7	0.9	1.4	
90–100	1.0	1.2	1.1	1.1	1.0	1.0	1.0	0.6	0.9	1.2	
100–110	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Urbic Technosols P21-39 (Zheleznodorozhny district)											
0–20	0.8	1.0	1.1	1.0	1.0	1.2	3.5	1.7	1.0	3.3	
20–50	1.0	1.2	1.1	1.0	1.1	1.1	1.9	1.6	0.9	1.4	
50–70	0.9	1.5	1.1	0.7	1.1	0.9	1.1	1.5	0.8	1.0	
70–90	0.9	0.9	1.1	1.0	1.1	1.0	1.0	1.2	0.9	1.0	
90–100	1.1	1.0	1.0	0.9	1.0	1.1	1.0	1.4	0.9	1.1	
100–120	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Urbic Technosols P21-40 (Leninsky district)											
0–25	0.4	0.5	0.5	1.1	0.5	1.3	4.3	0.8	1.4	1.2	
25–50	0.8	0.8	1.1	1.1	0.9	1.5	2.1	2.8	1.8	2.1	
50–70	0.4	0.5	0.9	0.8	0.7	1.7	1.3	3.5	1.9	2.3	
70–80	0.9	0.7	1.0	0.9	0.9	1.1	1.1	1.8	1.2	1.3	
80–110	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	1.0	
Urbic Technosols P21-44 (Proletarsky district)											
0–10	0.5	1.0	0.8	0.6	0.7	0.9	1.6	1.2	0.9	1.4	
10–30	0.8	1.0	1.0	0.7	0.9	1.0	1.1	0.9	1.1	1.5	

over the past years, due to a significant reduction in atmospheric and chemical loads, the boundaries of anomalously high concentration zones have become indistinct, and the area of metal distribution has increased (Privalenko and Bezuglova, 2003). The migration of zinc down the profile is noticeably reduced, due to its specific sorption by calcium and magnesium carbonates. Significant contamination of the lower part of the profile with zinc in urban stratozem on buried chernozem was recorded in borehole P21-49 at depths of 50–60 cm (1.8 APC) and 90–100 cm (3.5 APC). This phenomenon can be explained by the accumulation of this metal which had occurred even before the soil was buried under the technogenic horizon layer.

Regarding arsenic, the urbic horizons show levels that exceed the APC values for this metal in boreholes P21-39 (1.2 APC), P21-40 (1.7 APC), and P20-28 (1.4 APC). In this instance, the pollutant accumulates in the surface horizon, indicating ongoing contamination of soil by this element. Most likely, the metalloid enters the soil with atmospheric precipitation, which carries emissions from enterprises operating in the city. High arsenic concentrations are also recorded in the middle horizons of boreholes P21-49 (1.3 APC) and P20-24-1 (1.9 APC), which can be explained by chemisorption of the element on carbonate minerals.

Since the standards for chromium APC in soils have not been developed in Russia, it is rather difficult to judge the presence of local soil contaminations. The chromium content in soil depends on several factors, among which the following are usually emphasized: the mineralogical composition of soil, degumification processes caused by anthropogenic activities, and climatic conditions (Bugayev, 2015; Dubovik and Dubovik, 2016; Lukin, 2011; Lukin and Khizhnyak, 2016; Sergeev et al., 2017). This metal accumulation is recorded in the surface horizons, as well as in the middle and lower layers of the soil, while in the background areas of Rostov oblast, the content of chromium in the gross form can reach 250–300 mg/kg (Privalenko and Bezuglova, 2003). For this reason, in our opinion, it is most logical to conduct a qualitative assessment of the metal accumulation. The accumulation of chromium in the soil upper layers may be associated with the activities of machine- and instrument-making plants, burning of organic fuels, general degradation of soils in the residential area, which causes the release of chromium from humic acid complexes, and in the middle and lower layers – with the presence of secondary minerals in chernozems, for example montmorillonite, which is capable of adsorbing chromium on its surface.

Thus, it can be concluded that soils in the residential area, both native and anthropogenically altered, are characterized by a moderate degree of pollution and possess various barrier mechanisms that facilitate the maintenance of a stable ecological and geochemical state of buried chernozems. However, the migration of airborne and dust pollutants poses a risk to public health and can not only negatively impact living conditions of city residents, but also reduce the attractiveness of residential areas for investors.

To compare the distribution of heavy metals by depth in natural and anthropogenically transformed soils, data on the gross content of zinc, copper, and lead – the main pollutants that significantly impact vegetation – were statistically processed. Range (Fig. 2) and scatter (Fig. 3) diagrams were constructed, which demonstrate a fairly large variation in values for urban horizons in residential areas compared to natural soils. The element concentrations in buried horizons are comparable to the corresponding concentrations in the horizons of natural soil. However, urban horizons are characterized by high levels of pollution. In natural soils, a direct correlation was found between the copper content and the soil horizon depth. An inverse correlation was observed for zinc and lead (Table 6).

From an ecological standpoint, the impact on phytocenosis is exerted not so much by an increase in the content of heavy metals in gross forms, but rather by their enhanced mobility in soils. High concentrations of copper in the exchangeable form are observed in almost all urban horizons (Fig. 4); in addition, peaks are also recorded in the underlying layers, which can be explained both by the involvement of soil organic substances in the interaction with copper and by the specific sorption of copper by carbonate minerals. Local zones of high-contrast pollution at a depth of 0–25 cm in borehole P21-40 (5.6 APC) and a depth of 20–50 cm (16.4 APC) and 50–60 cm (16.2 APC) in borehole P21-49 indicate the technogenic nature of pollution and, consequently, the presence of toxic concentrations of copper ions in the soil (Table 7). At the same time, there is a tendency for the metal content to decrease in the underlying horizons.

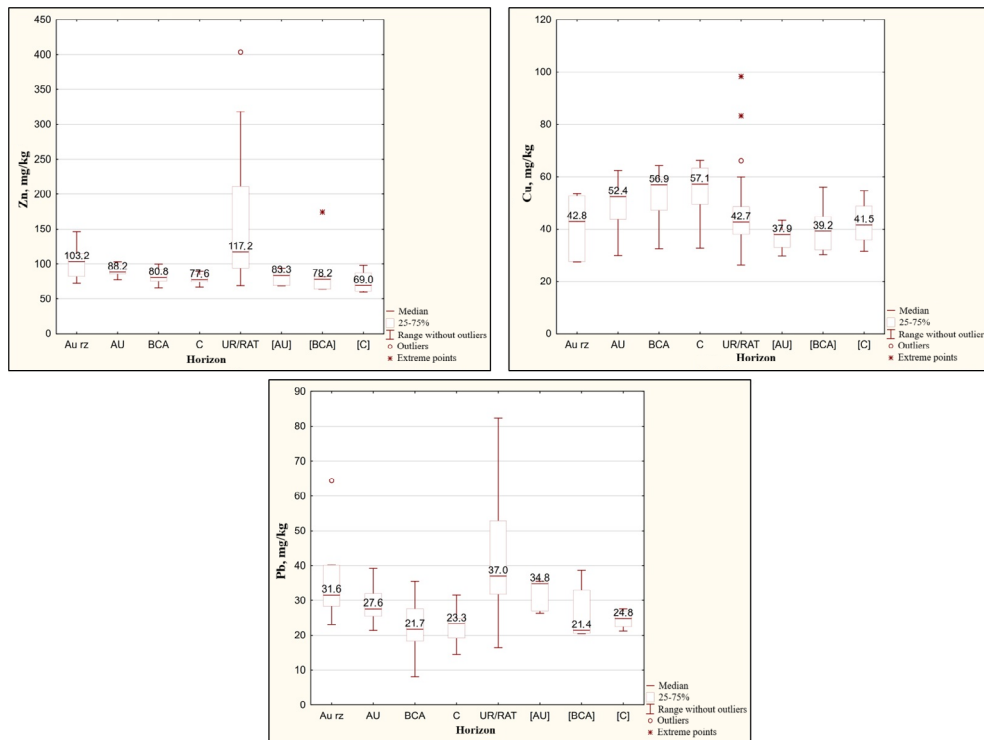


Fig. 2. Range diagrams for the content of gross forms of zinc, copper and lead in soil horizons of Rostov-on-Don. AU rz – humus-accumulative (sod) horizons with humus content above 5%; AU – humus-accumulative horizons with humus content below 5%; BCA – accumulative-carbonate horizons; C – soil-forming rock; UR/RAT – horizons of anthropogenically transformed soils; [AU], [BCA], [C] – analogues of native horizons buried under anthropogenic strata.

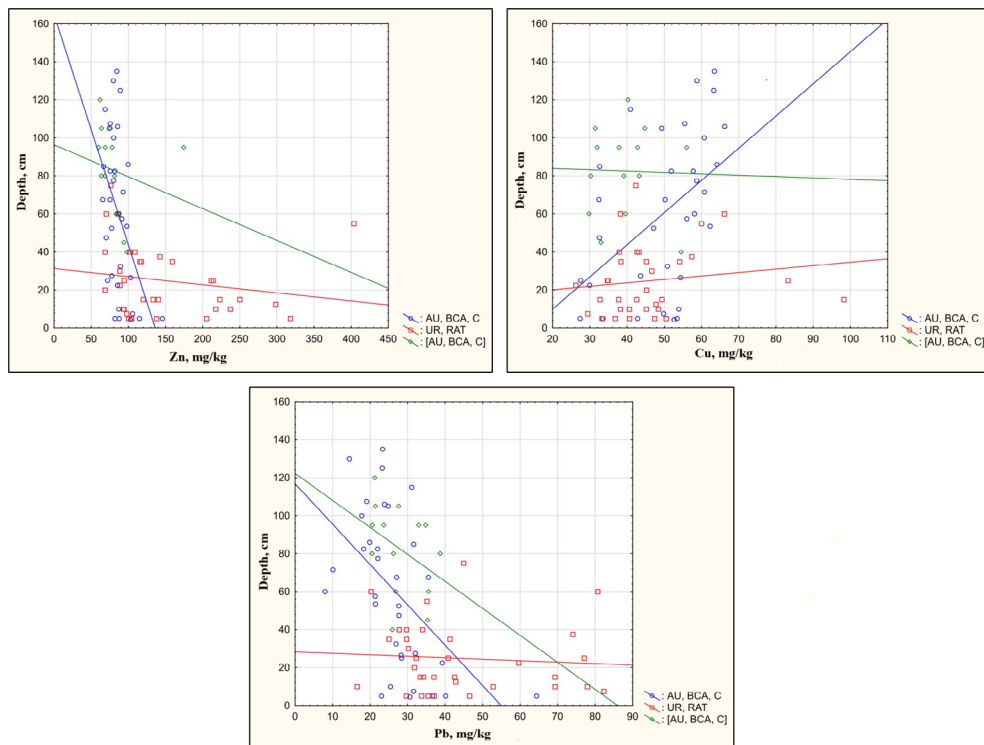


Fig. 3. Scatter diagrams for zinc, copper and lead in a group of soil horizons of Rostov-on-Don. AU, BCA, C – horizons of natural soils; UR/RAT – horizons of anthropogenically altered soils; [AU], [BCA], [C] – analogues of native horizons buried under anthropogenic strata.

Table 6. Statistical parameters (r – correlation coefficient; p – confidence level) of scatter diagrams for the content of gross forms of zinc, copper and lead in a group of soil horizons of Rostov-on-Don. AU, BCA, C – horizons of natural soils; UR – urbic horizon of anthropogenically transformed soils; [AU], [BCA], [C] – analogues of native horizons buried under anthropogenic strata.

Horizons	Statistical parameter	
	r	p
	Cu	
AU, BCA, C	0.4788	0.0048
UR	0.1416	0.4320
[AU], [BCA], [C]	0.0249	0.9325
	Zn	
AU, BCA, C	-0.4652	0.0064
UR	-0.1889	0.2924
[AU], [BCA], [C]	-0.2057	0.4805
	Pb	
AU, BCA, C	-0.5161	0.0021
UR	-0.0792	0.6613
[AU], [BCA], [C]	-0.3816	0.1782

The presence of local foci of zinc pollution with levels exceeding the APC values by 1.1–2.0 times suggests the presence of a significant proportion of exchangeable forms of this metal in the soil. However, it has been shown that zinc mobility in urban stratozems and urban stratified chernozems is rather low. This phenomenon can be attributed to two factors: firstly, the active absorption and accumulation of zinc exchangeable forms in the assimilating organs of plants, since samples were taken under herbaceous and woody cenoses; secondly, the predominance of strongly bound metal forms in the soil, due to the carbonate mineral content of the substrate.

The accumulation of lead in the surface layer of urban is largely related to the traffic density in residential areas (Aslam et al., 2013). The content of this element in the bulk form does not exceed the APC values in Rostov agglomeration; however, there are zones of increased concentrations of its mobile forms in the surface layer, which may be associated with active processes of the metal complexation with soil organic matter. Pockets of contamination were found at the carbonate barrier level in boreholes P21-46 (14.5 APC) at a depth of 65–90 cm and in boreholes P21-40 (5.3 APC) at a depth of 0–25 cm.

Statistical processing of data on the distribution of mobile forms of zinc, copper, and lead at different depths of the profile does not allow us to find a correlation. This is probably due to the combination of soil properties that affect the mobility and, consequently, the distribution of metals within the profile, which is reflected in the large number of outliers in the analyzed samples (Fig. 4).

The foci of contamination of synlithogenic soils with metals in both gross and mobile forms indicate that transformed soils of residential areas have signs of contemporary as well as historic anthropogenic impacts. In a number of samples, elevated zinc concentrations are found in soils shielded by asphalt pavement, which indicates that this metal entered the soil in those years when the largest in the USSR producer of zinc whitewash, named after the October Revolution, was located almost in the center of the sprawling city. In the 1990s, the plant was transformed into JSC Empils, and its main production was relocated to the outskirts of Zapadnyy microdistrict. Considering the wind rose (predominantly eastward), the uppermost soil horizons are currently not contaminated with zinc.

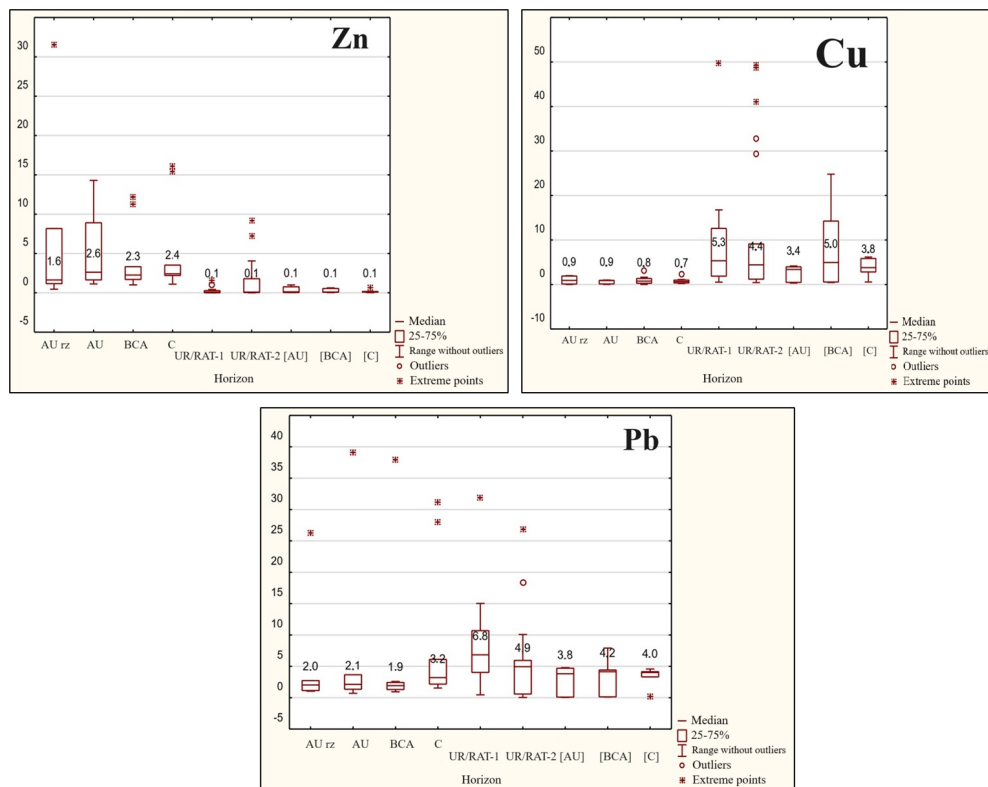


Fig. 4. Range diagrams for the content of mobile forms of copper, zinc and lead in soil horizons of Rostov-on-Don. Notation as in Fig. 2.

Conclusion

The diagnostics of native and anthropogenically transformed soils, carried out in this study, provide insight into the spatial structure of heavy metal pollution in residential areas of the city. Urban horizons of urban stratozems and urban stratified chernozems, which primary pollutants are zinc and arsenic (their concentrations do not exceed two APC), are subject to the greatest anthropogenic load. Nevertheless, from a sanitary and hygienic standpoint, these urban soils are generally characterized by an acceptable level of pollution – $Z_c < 16$. The exception is borehole P20-28 at a depth of 0–10 cm, where the level of pollution is categorized as moderately hazardous ($Z_c = 16.8$).

The large amount of copper in exchangeable form in the soils of urbanozems is noteworthy. However, the distribution of this metal along the profile indicates the pedogeochemical specifics of urban landscapes rather than the fact of contamination. Nevertheless, localized areas with abnormally high concentrations of copper ions (16.6 MPC) and lead (5.3 APC) were found, suggesting the technogenic nature of upper horizons pollution.

Despite the fact that APC levels of pollutants in the transformed soils of residential areas are exceeded, the presence of urban horizons, often characterized by a higher density, and carbonate barriers in buried chernozems slow down the migration of metals deep into the profile, mitigating anthropogenic load on chernozems.

Natural migration-segregation chernozems are the cleanest soils in the city. However, the proximity of some territories to pollution sources significantly affects the accumulation of pollutants such as zinc and lead in humus-accumulative horizons.

In summary, the study has shown that the soils in residential areas of Rostov-on-Don are characterized by a moderate level of pollution with heavy metals; however, some territories require remediation measures to prevent soil degradation.

Table 7. Hazard coefficient (K_h) values of mobile forms of metals in anthropogenically transformed soils.

Depth, cm	Element		
	Cu	Zn	Pb
Urbic Technosols P20-37			
0–10	0.24	0.04	0.48
10–20	0.22	0.08	0.27
20–30	0.22	0.13	0.10
30–40	0.23	0.32	0.08
40–50	0.16	0.04	0.02
50–70	0.11	0.03	0.01
70–90	0.15	0.03	0.02
90–100	0.19	0.02	0.02
100–110	0.19	0.03	0.03
Urbic Technosols P21-39			
0–20	3.70	0.00	2.51
20–50	2.14	0.00	0.90
50–70	1.43	0.01	0.55
70–90	1.68	0.00	0.74
90–100	2.06	0.00	0.76
100–120	1.95	0.01	0.67
Urbic Technosols P21-40			
0–25	5.59	0.00	5.32
25–50	2.55	0.00	3.05
50–70	3.04	0.01	4.48
70–80	1.24	0.00	1.00
80–110	1.32	0.01	0.78
Urbic Technosols P21-44			
0–10	1.01	0.01	1.59
10–30	2.27	0.00	1.12
30–50	1.09	0.00	0.84
50–70	1.39	0.00	0.64
70–90	1.13	0.00	0.80
90–120	0.94	0.00	0.69

Depth, cm	Element		
	Cu	Zn	Pb
Urbic Technosols P21-46			
0–20	4.70	0.00	1.32
20–40	2.11	0.00	0.81
40–65	1.62	0.01	0.82
65–90	1.34	0.00	14.53
90–120	1.47	0.00	0.75
Urbic Technosols P21-49			
0–20	1.81	0.00	0.96
20–50	16.46	0.00	0.84
50–60	16.24	0.01	0.86
60–90	8.26	0.00	0.66
90–100	4.75	0.00	0.71
Urbic Technosols P20-24-1			
0–10	1.75	0.00	0.57
10–20	0.78	0.00	0.68
20–30	1.65	0.01	1.32
30–50	1.26	0.00	0.55
Urbic Technosols P20-28			
0–10	16.60	0.00	1.97
10–20	13.67	0.00	0.90
20–30	9.77	0.00	0.99
30–50	10.95	0.00	0.70

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