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APPLIED PROBLEMS
OF ARID LANDS DEVELOPMENT

Specific Features of Content and Mobility of Heavy Metals in Soils of Floodplain of the Don River

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Abstract—The gross heavy metal contents were studied in the main soil types of the floodplain of the estuarine segment of the Don River. The ratio of elements strongly bound to soil components to those that are weakly bound was determined for the first time. It was established that geochemical features of the fixation and distribution of elements in compound forms in the studied soils are determined by the soil buffering capacity, the chemical properties of the elements themselves, and their association with sources of anthropogenic emission.

Keywords: heavy metals, soils, gross content, weakly bound compounds, mobility, pollution

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INTRODUCTION

The floodplain of the estuarine region of the Don River is located in a semiarid climate. It is unique for the productivity of the territory, which is characterized by extremely favorable natural conditions. The high soil fertility and hydrological regimen of Don River have resulted in the formation of a highly productive meadow biocenosis of the floodplain and deltaic landscapes that serve as spawning areas for valuable fish breeds. At present, this territory is affected by active technogenic influences. The mostly important, in terms of its consequences, was the overregulation of the Don River runoff. The estuarine ecosystems serve as natural barriers, accumulating substances carried by the water, including contaminants. The cities of Rostov-on-Don, Novocherkassk, Azov, and Bataisk are located in the Don River estuarine region, as are large industrial establishments that emit large amounts of contaminant substances to the atmosphere. Emissions by a JSC OGK-2 affiliate, the Novocherkassk power station (NPS), make up to 1% of the total emission of polluting substances into the Russian air and up to 99% of the aerosol emissions in Rostovskaya oblast (*Ekologiya*...,, 2001). As a result of the location of the main sources of air pollution and the dominant wind direction, a substantial portion of the fallout precipitates within the floodplain of river estuarine region (Fedorov et al., 2012).

Research on the concentration and migration of chemical elements in the floodplain soils and their influence on crop capacity has been conducted in the past and is being conducted at present. A substantial number of works is dedicated to the geochemistry of heavy metals (HMs) in the studied region (Alekseenko, 2002; Minkina et al., 2008a, 2008b, 2009, 2013; Fedorov et al., 2012; etc.). Despite the collected material, many questions on the accumulation, dispersion, and transformation of HMs in soil cover of the Don River estuarine region remain unsolved. Thus, this work is relevant.

The purpose of this work was to study specific features of the accumulation and distribution of the gross content and mobile forms of HMs in soils of the estuarine ecosystems of the floodplain and deltaic landscapes of the Don River.

MATERIALS AND METHODS

From the viewpoint of geomorphology, the studied territory is confined to the Don River floodplain; as for hydrology, it is situated within its present estuarine region, the upper limit of which passes in range of Razdorskaya stanitsa (Gar'kusha and Fedorov, 2010). In turn, the delta is a part of the Don River estuarine region; the soil studies were mainly conducted in the floodplain of this region.

Monitor stations were installed to study specific features of the geochemical condition of the soil cover in landscapes of the estuarine region floodplain (Fig. 1). The soil cover on the examined ground is represented by meadow, alluvial-meadow, saturated, and alluvial-stratified soils underlaid with alluvial sediments. Soil samples were taken from a depth of 0–20 cm. According to the guidelines (*Agrokhimicheskie*..., 1975) the main physico-chemical attributes of soils were estimated: granulometric soil compound, organic matter content, carbonates, exchangeable Ca^{2+} and Mg^{2+}, pH, and dense water extract residue.

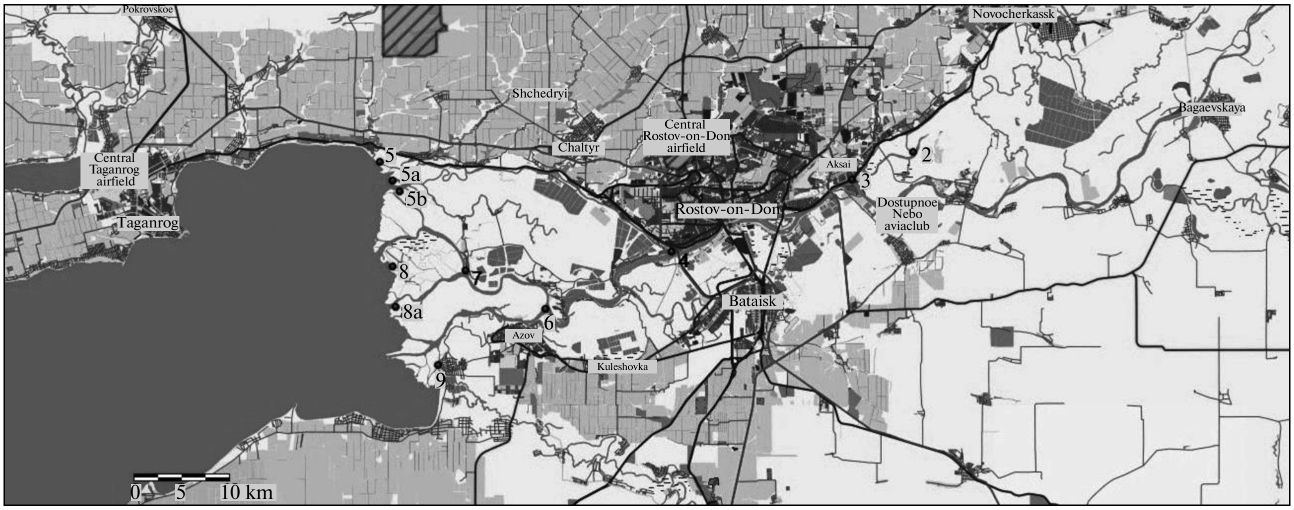

Fig. 1. Location of monitoring stations in the floodplain and delta of the River Don. The structure of the soil covers on the test stations: 1—low-humus, light loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 2—low-humus, light loamy, saturated, meadow, reclaimed alluvial soil on alluvial deposits (L); 3—low-humus, clay, loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 4—low-humus, light sandy, saturated, alluvial-stratified soil on alluvial deposits (AS); 5—low-humus, sandy, saturated, alluvial, meadow soil on alluvial deposits (AL); 5a—low-humus, light loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 5b—low-humus, light loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 6—low-humus, light loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 7—low-humus, sandy, loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 8—low-humus light loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 8a—low-humus, sandy, loamy, saturated, alluvial, meadow soil on alluvial deposits (AL); 9—low-humus, light loamy, saturated, alluvial, meadow soil on alluvial deposits (AL).

The condition of the examined soils was assessed by the value of the gross content of chemical elements in soils and by indices of the soil retention strength of metals and metalloids. The gross content of Mn, Cr, Ni, Cu, Zn, Pb, Cd, and As in soils was determined by X-ray–fluorescent technique and expressed in mg/kg.

In the analysis of the metal compound composition, the focus was on the ratio of metal compounds that were strongly bound to soil components to those weakly bound. This determines the ecological consequences of the metal pollution of soils and leads to practical interest in the development of different mechanisms for metal detoxication in soils, because certain solid mineral and organic soil phases have a high buffering capacity for a wide range of soil contaminants, thus providing a protective function for soil.

Weakly bound metal compounds include external-sphere metal complexes accompanied by a variety of functional groups of solid soil phases. Strongly bound metal compounds, which result from the formation of internal-sphere complexes with solid phases, are non-ventilated, original minerals. We propose the use of the content of weakly bound HM compounds in soil as an integral indicator of metal mobility and the capability to participate in mass transfer processes (Mandzhieva et al., 2014).

Weakly bound HM compounds in soils include exchangeable, complex, and specifically sorbed compounds, the content of which in soil is tightly associated with their content in plants (Minkina et al., 2014). HM compounds labeled as weakly bound are transferred into a solution by parallel extractions by reagents (Minkina at al., 2013).

(1) 1 N ammonium-acetate buffer (NH_4Ac) with a pH of 4.8 (soil-to-solution ratio of 1 : 10 and extraction time of 18 h), able to transfer exchangeable metal forms into a solution, which characterizes their "actual" mobility.

(2) 1% EDTA NH_4Ac solution with a pH of 4.8 (soil-to-solution ratio of 1 : 10 and extraction time of 18 h), which allegedly, along with exchangeable metal forms, transfers their complex compounds into a solution.

By the difference between the metal content in EDTA extract in NH_4Ac and NH_4Ac, we calculated the metal content found in the composition of complex compounds (Nosovskaya et al., 2001, Protasova and Gorbunova, 2006).

(3) acid-soluble metal forms derived with 1 N HCl solution (soil-to-solution ratio of 1 : 10 and extraction time of 18 h), which characterizes the potential reserve of mobile compounds in soil. They are supposedly represented by exchange-capable metal ions and specifically retained compounds, including those retained by amorphous Fe and Mn oxides and carbonates.

We calculated the number of specifically retained metal compounds from the difference between the metal compounds in HCl and NH_4Ac extracts. The additivity of extracts is experimentally proven (Minkina et al. 2014). The metal content in extracts is

Table 1. Physicochemical soil properties of monitoring stations of the estuarine ecosystem of the floodplain and delta of the river Don (0–20 cm layer)

Station No.	Soil	Humus, %	pH	$CaCO_3$, %	Dense residue, %	Exchangeable bases, mmol (+)/100 g		Size (mm) and contents (%) of organic fractions		
						Ca^{2+}	Mg^{2+}	<0.001	<0.01	name by granulometric content
1	AL	3.03	7.78	2.80	0.045	27.1	2.1	9.71	29.02	Light loam
2	L	1.88	7.67	4.43	0.086	16.0	3.0	13.90	26.40	Light loam
3	AL	2.30	7.93	0.18	0.035	33.0	6.0	27.00	47.70	Heavy loam
4	AS	0.22	8.00	0.18	0.002	1.00	0.5	0.10	0.30	Loose sand
5	AL	1.23	7.60	8.70	0.184	17.0	3.0	0.20	6.30	Cohesive sand
6	AL	0.43	7.42	0.32	0.138	30.0	6.0	10.90	23.40	Light loam
7	AL	1.30	7.76	0.02	0.034	17.0	3.0	7.60	14.00	Sandy loam
8	AL	1.66	7.25	0.43	0.040	27.0	2.0	11.00	24.70	Light loam
8a	AL	0.40	8.06	0.64	0.081	34.0	7.1	7.40	14.00	Sandy loam
9	AL	2.14	8.91	0.47	0.075	18.0	3.0	21.50	29.10	Light loam

AL—alluvial-meadow soil, L—meadow soil, AS—alluvial-stratified soil.

estimated by atomic absorption spectrophotometry (AAC).

The HM content in the composition of strongly bound compounds was estimated by the difference between the gross metal content in the soil and the content of their weakly bound compounds.

RESULTS AND DISCUSSION

Comparison of the results of chemical analyses of meadow, alluvial-meadow, and alluvial-stratified saturated soils from the examined monitor stations (Table 1) demonstrates that the granulometric compound of the soil is rather mixed and is re presented mainly by sandy, sabulous, and light-loamy species. Fractions of fine and medium sand are predominant. The examined soils have neutral, alkalescent, or strongly alkaline medium reactions (7.3–8.9) and a low humus content of 0.2–3.7, which was mainly determined by the qualitative content of the infused and redeposited material composing the inwashed and buried horizons. The overwhelming majority of the examined soils are not saline (the value of dense residue does not exceed 0.15%). The high carbonate content from soil covers in some stations is associated with the presence of biogenic calcite in deposited horizons. Calcium predominates in the composition of the absorbent complex (Table 1).

The gross soil analysis makes it possible to trace changes in the chemical composition of the most stable part of soils, the minerals. A macroelement analysis of soils showed that the SiO_2 content at stations 1, 4, 5, 7, 8a, which have a lite granulometric composition, is increased relative to the amount of R_2O_3 and other oxides, which contain primary nutritional elements: CaO, MgO, and K_2O (Fig. 2).

The accumulation and distribution of HM in soils is determined by external and internal factors. The external factors are conditioned by physico-chemical properties of soils, the geomorphological features of the examined territory, and the association with sources of technogenic emission. The internal factors are related to the atomic properties of chemical elements and their compounds (Minkina et al, 2003; Violante et al., 2007). A complex of physico-chemical parameters directly performs soil-protector functions. To reveal them, it is necessary to assess the soil protective abilities (buffering capacity) for HMs.

The buffering capacity of the examined soils in the Don River floodplain was assessed according to technique of V.B. Ilyin (1995), which is based on an accounting of the inactivation capability of soil characteristics: humus, physical clay, carbonates, sesquioxides, and pH.

Assessment of the soil buffering capacity has shown that it is somewhat different in the studied soils (Fig. 3). The major factors in the formation of the buffer value of the studied soils for HMs are physical clay, carbonates, and humus. The contribution of pH and sesquioxides is practically constant for the studied objects. According to the buffering capacity gradation for HMs, alluvial-stratified, sandy soil (station 4) and alluvial-meadow, sandy-loam soils (stations 7 and 8a) have a medium degree of this parameter, while the highest buffering capacity index characterizes meadow, light-loamy soil (station 2). The soils can be arranged by the buffering capacity value for HMs in descending order: meadow alluvial-deposited light-

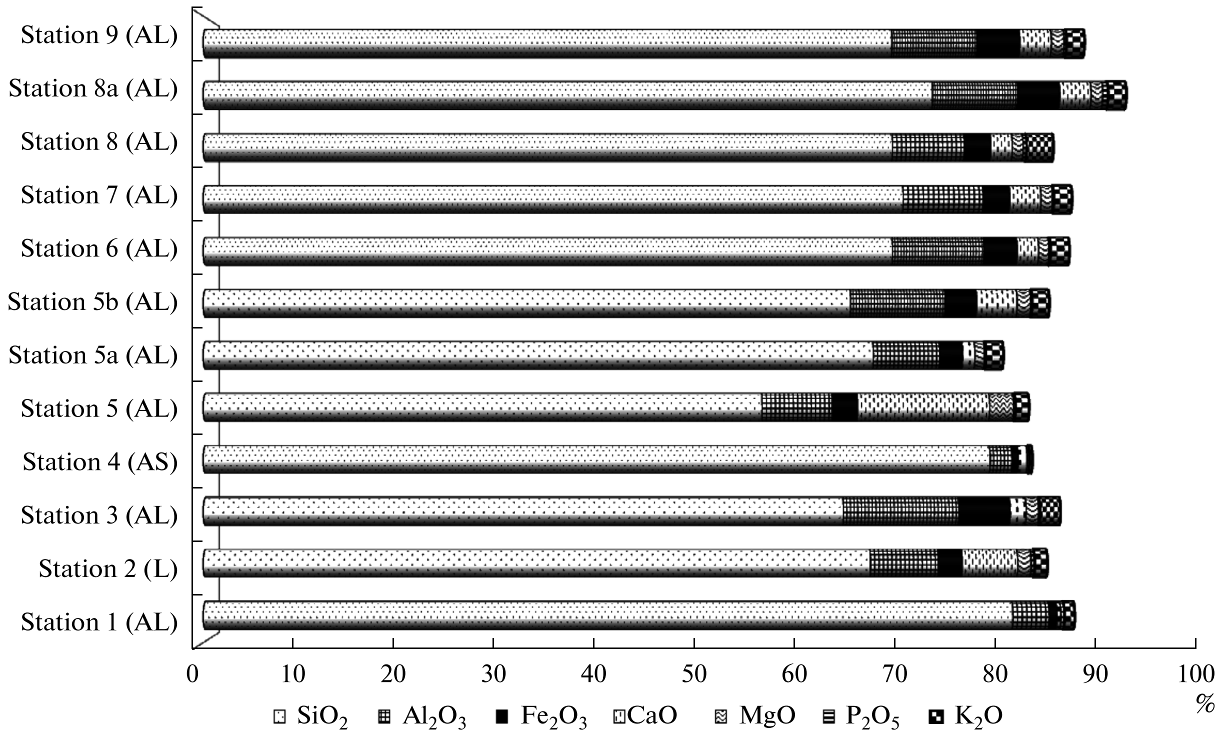

Fig. 2. Concentration of macroelement oxides in test station soils in the floodplain and delta of the river Don.

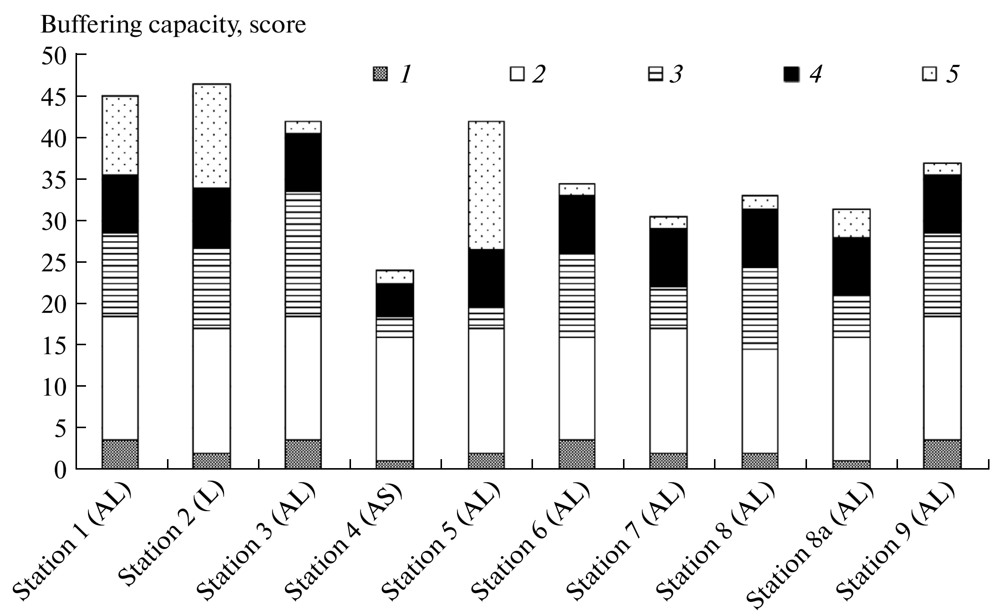

Fig. 3. Buffering capacity of floodplain soils of the river Don in relation to heavy metals. Points obtained by *1*—humus, *2*—pH, *3*—physical clay, *4*—R_2O_3, *5*—CO_3^{2-}.

loamy ≥ alluvial-meadow light-loamy > alluvial-meadow heavy-loamy > alluvial-meadow sandy and sandy-loam > alluvial-stratified sandy.

The intensity of the accumulation and distribution of HMs in soils is directly determined by the ecological conditions of their formation and buffering capacities. High values for the soil content of humus and clay particles facilitate active metal accumulation (stations 1, 3, 8, 9). In sandy-loam and sandy, alluvial-meadow, saturated, and alluvial-stratified saturated soils (stations 4, 5, 7, 8a), hydrogenic accumulation processes take primary importance, but the HM content in such soils is low because of the low soil humus content and the low content of absorbed cations, clay particles, and other factors (Table 1, Fig. 3).

Below, let us consider the distribution of gross HM content in the soils of the monitor stations, which is presented in Fig. 4.

Manganese. In the soils of the monitor stations, the manganese content changes from 469.8 to 1910.0 mg/kg (Fig. 4). In work of Cherkashina et.al (1998), it was established that the manganese content in pedogenic species and floodplain and delta soils varies within wider limits, from 100 to 2000 mg/kg. Meanwhile, the maximum manganese content is associated with soils with predominance of a 0.005–0.05 mm fraction and a high organic matter content. A distinct connection between the manganese concentration and landscape relief also appears—the relatively low contents (200–300 mg/kg) are associated with “sandy” ridges, while the concentration increases to 600–800 mg/kg in interridge depressions. On average, the manganese contents in pedogenic species of the floodplain and delta is 300 and 400 mg/kg (Luk’yanchenko at al., 2001). The highest manganese concentration is associated with the meadow soil of the floodplain (station 2). Moreover, an excess of manganese clarke and MPC, constituting 850 mg/kg and 1500 mg/kg, respectively, is observed (Vinogradov, 1857).

Chromium. The chromium content varies from 51.2 to 121.4 mg/kg of soil. In pedogenic species of the Don River floodplain and delta, the chromium content is 69 mg/kg and 97 mg/kg, respectively. On many grounds, an excess is observed not just in background values but also in the MPC of this element (Fig. 4). In the soil, chromium is multivalent with a predominance of poorly soluble compounds. Most of the chromium is present in the form of Cr^{3+} as a part of minerals or in the formation of different oxides, displaying an affinity with iron-containing phases in soils. Siderite (38–76%) and ferric hydroxides (15–25%) account for a significant part of the heavy fraction content of the Don River floodplain and delta soils (Luk’yanchenko et al., 2001).

Nickel. The amount of nickel in the soils of deltaic landscapes is below the clarke values of the lithosphere, 41.8 mg/kg and MPC. However, in floodplain landscape soils, the nickel content reaches 45.6–60.9 mg/kg, which exceeds the nickel concentration in pedogenic species of the floodplain (16 mg/kg) and delta (37 mg/kg). Nickel is mainly retained by hydroxides and ferric and manganese oxides (Minkina et al., 2013).

Copper. Copper is characterized by high organophilic qualities and is related to strong complexing agents, being fixated in the soil in the form of strong organic chelates. The amount of copper in the organogenic layer of the examined soils varies from 12.3 to 60.9 mg/kg (Fig. 4). Pedogenic species of Don River floodplain and delta contain 21 mg/kg and 41 mg/kg of this element. The copper content in the Don River floodplain soils is notable for its quite high values, in some cases exceeding the MPC (Fig.4).

Zinc. In pedogenic species of the floodplain and delta, the zinc content is 49 mg/kg and 84 mg/kg, which corresponds to the lithosphere clarke (according to Vinogradov (1957), the Zn clarke equals 50.0 mg/kg of species), background (72 mg/kg), and MPC (100 mg/kg). The high zinc content characterizes the soils with the most humus, those of stations 6, 1 and 3, which represent the biogenic accumulation of metal in the humus horizons.

Lead. In pedogenic species of the floodplain, lead is 14.0 mg/kg on average and 35.0 mg/kg in deltaic species, which is higher than lead clarke (10 mg/kg). In the soils of the examined objects, the lead contribution varies widely, ranging from 2.5 to 33.0 mg/kg. The maximum metal concentrations are registered in monitor stations 1, 3, 5, and 5a.

Cadmium. In nature, cadmium appears in the form of small particles near smelting plants, and from there they travel into the atmosphere, soil, and water. Cadmium is not found in pedogenic species (Luk’yanchenko et al., 2001). A small amount (0.4 mg/kg on average) is registered in the upper soil layer. Apparently, this can be explained by aerogenic pollution of the floodplain and deltaic landscapes by cadmium.

Arsenic. The main contribution of arsenic in the Don River floodplain and deltaic landscape ecosystems is associated with coal combustion products, waste products of the metallurgy industry, and the usage of arsenic-containing pesticides. The arsenic contribution in the soil ranges from 6.2–11.6 mg/kg, which is several times that of the MPC and background values (Fig. 4). The degree of arsenic pollution in the soils fluctuates from weak to strong. Meanwhile, arsenic accumulation, in addition to external factors (the presence of pollution sources), can be caused by its chemical properties and the ability to change its allotropic form in fluctuations of redox conditions. The background content (4.8 mg/kg) and arsenic clarke (5.0 mg/kg) in soil is 2.5 times higher than the MPC.

The studied HMs can be represented in sequentially descending order by their gross content in the soils of the monitoring stations in the floodplain and deltaic landscapes of Don River estuarine ecosystems: Mn > Cr > Z > Ni > Cu > Bb > As > Cd.

The assessment of soil pollution by the gross metal content does not allow a determination of mobility or the ability to transfer to adjacent media, primarily, into plants and natural waters. The content of weakly bound HM compounds in the soil is more informative (Minkina et al., 2013). The amount of weakly bound HM forms varies from 18% in meadow soil to 81% in alluvial-stratified soil, depending on the metal (Fig. 5). In floodplain landscape soils, the content of weakly bound compounds is 30–83% of the total content, on

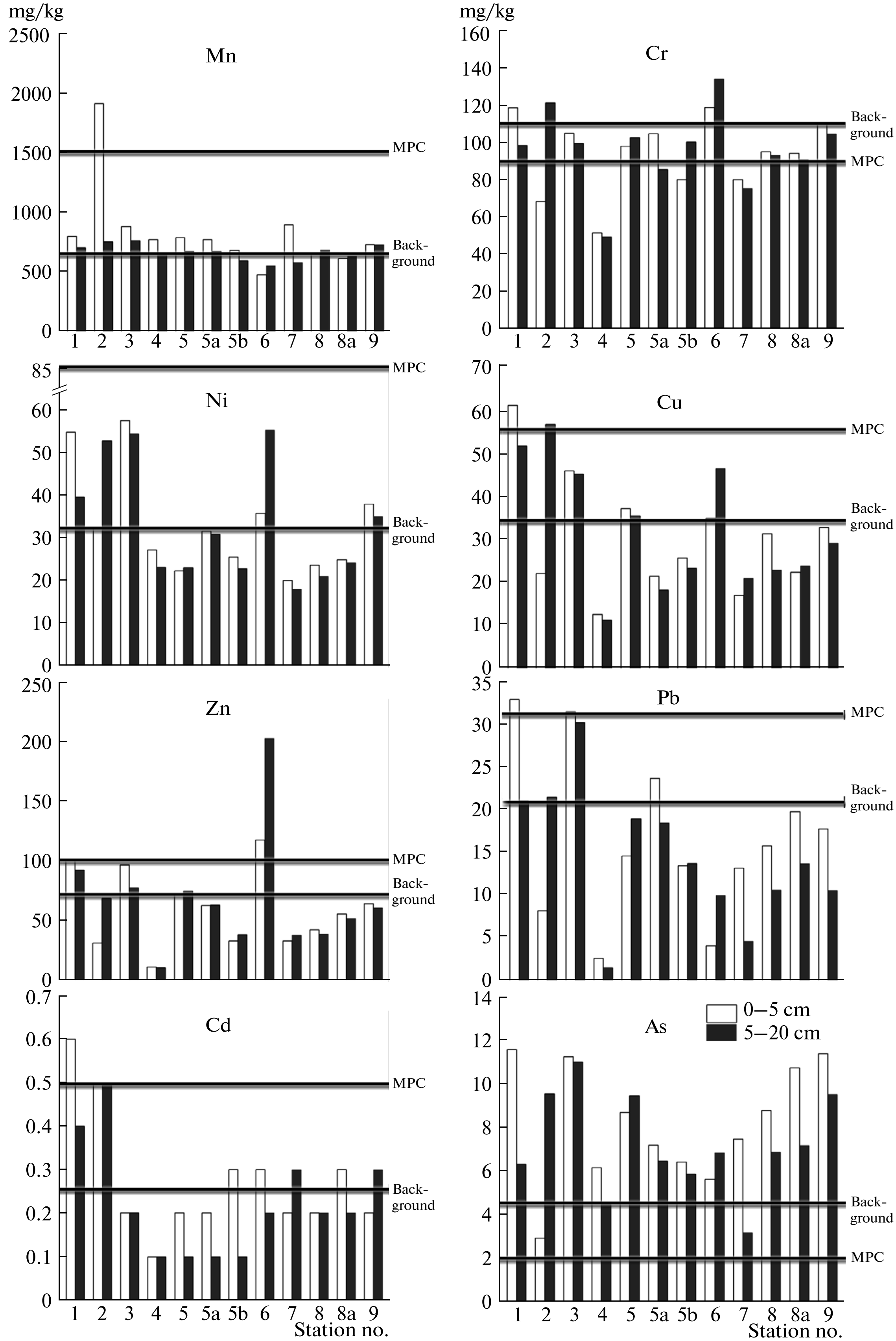

Fig. 4. Total content of heavy metals in the soils of monitoring stations for the estuarine ecosystem floodplain of the River Don by layers, mg/kg.

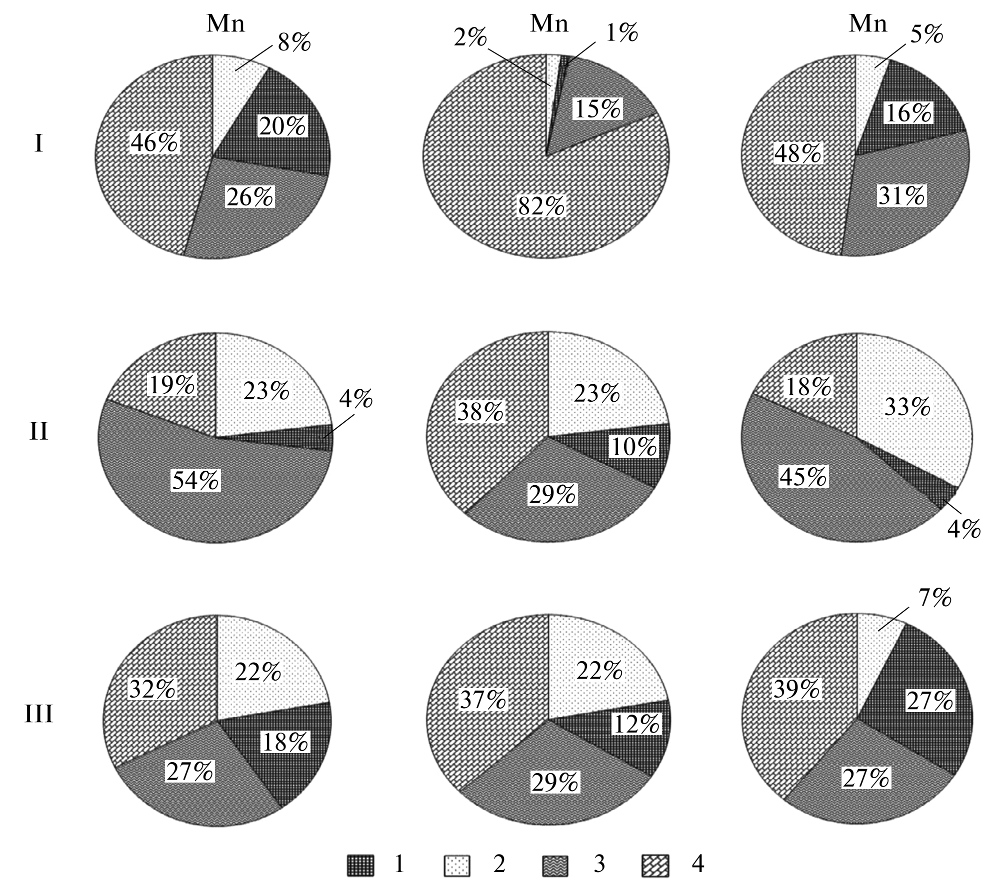

Fig. 5. Content of loosely bound compounds (exchangeable, complex, specifically sorbed) and strongly bound compounds Mn, Zn, and Pb in soils of the floodplain and delta of the river Don, % of the total: I—meadow soil (station no. 2); II—alluvial-stratified soil (station no. 4); III—alluvial meadow soil (station no. 6). 1—exchangeable forms, 2—complex forms, 3—specifically sorbed forms, 4—strongly bound forms.

average, which strongly distinguishes them from zonal common chernozem soils, in which weakly bound compounds constitute only 10–20% (Table 3). The contribution of weakly bound HM compounds is highest on the sandy soils of ground 4, which is linked with a low content of humus and clay particles, which are capable of retaining HMs (Fig. 5, Table 1). Thus, with a decrease in the soil buffering capacity, the contribution of weakly bound compounds increases, i.e. their mobility grows.

The contribution of strongly bound HM compounds varies greatly (from 18 to 82%) depending on examined soils of monitor stations (Fig. 5) and is mainly limited by the content of the fine-dispersed fraction. Of the total reserve of strongly bound HM compounds in soils, 69–74% are metals in silicate structures. The pollution level increases the amount weakly bound metal compounds, because the formation of extra amounts of mobile metal forms is observed in polluted soils (Mandzhieva et al. 2014).

Metals form the following ascending series by the soil content of weakly bound (% of total content): Cd > Pb > Mn > Zn > Cu > Ni. The contribution of weakly bound HM compounds is highest at monitor stations 1, 4, 5, and 6. As Mazhaysky et al. (2003) noticed, with large waste capabilities, the degree of mobility can reach 73–83%. Regional characteristics of HM behavior in Lower Don floodplain and delta soils include the weakly bound compounds Cd, Pb, Mn, Cu, Ni, which are represented mainly by specifically absorbed forms on carbonates and Fe–Mn (hydr)oxides.

The content of the most mobile exchangeable forms is practically heterogeneous, from 1 to 63%, in the studied soils and directly depends on their buffering capacities and properties of chemical elements (Table 2, Fig. 5)

A wide range in the content of exchangeable zinc forms is registered in the examined station soils (up to 30-fold). Mobile (exchangeable) Zn compounds slightly exceed the MPC in the soils of monitor stations 1 and 6 (Table 2, Fig. 5).

The amount of exchangeable Cu forms is also insignificant and does not exceed the MPC, except for the most polluted monitor station (1), which is located

Table 2. Content of exchangeable, complex, and specifically sorbed forms of Mn, Ni, Cu, Zn, Pb, and Cd in the 0–20 cm soil layer of the floodplain and delta of the river Don mg/kg

Station No.	Soil	Mn			Ni			Cu			Zn			Pb			Cd		
		exchangeable	complex	specifically sorbed	exchangeable	complex	specifically sorbed	exchangeable	complex	specifically sorbed	exchangeable	complex	specifically sorbed	exchangeable	complex	specifically sorbed	exchangeable	complex	specifically sorbed
1	AL	133.8	165.0	231.4	1.7	5.3	12.4	**3.2**	4.6	10.7	**23.6**	3.9	23.7	3.1	3.6	5.7	**0.09**	0.08	0.2
2	L	106.3	265.5	341.7	1.1	2.3	5.3	0.6	2.2	8.1	1.2	0.6	7.5	0.8	2.4	4.5	**0.08**	0.02	0.1
3	AL	118.3	33.6	121.8	1.7	4.1	5.6	0.8	3.6	9.5	5.8	2.1	13.9	2.1	3.7	4.1	**0.09**	0.02	0.09
4	AS	13.6	2.5	32.2	0.7	0.4	1.0	0.4	1.0	5.2	2.3	1.0	2.9	1.5	0.2	2.0	0.01	0.01	0.01
5	AL	90.2	72.0	147.7	1.2	0.8	1.7	0.8	2.6	7.8	13.0	7.9	17.8	1.6	2.5	4.7	**0.18**	0.01	0.1
5a	AL	34.7	56.0	143.4	0.7	0.9	2.9	1.3	3.8	5.9	2.4	6.6	13.0	1.2	1.9	3.6	0.01	0.01	0.04
5b	AL	40.0	51.5	63.9	0.9	0.9	4.4	1.1	5.2	5.8	5.7	2.3	7.8	0.8	2.5	3.9	0.03	0.04	0.07
6	AL	113.6	88.8	139.1	1.0	1.8	3.9	1.0	9.5	14.2	**37.6**	20.0	49.2	0.8	2.9	3.0	**0.38**	0.02	0.1
7	AL	34.5	56.7	99.0	1.0	1.9	5.2	0.4	2.7	9.3	3.0	2.1	11.0	1.9	3.0	3.32	**0.07**	0.05	0.07
8	AL	48.5	54.2	123.9	1.3	1.0	3.1	0.7	1.3	8.4	5.6	3.2	8.7	1.3	3.9	4.1	0.04	0.03	0.06
8a	AL	65.9	67.3	156.2	1.2	1.2	4.7	0.7	4.3	10.1	5.1	3.7	15.1	2.5	3.8	4.5	0.04	0.02	0.02
9	AL	67.0	76.9	120.4	2.0	3.3	4.3	0.6	2.8	4.6	3.7	5.1	10.1	1.0	3.8	4.1	0.04	0.07	0.12
$LSD_{0.5}$ (least significant difference)		4.0	3.5	4.5	0.1	0.2	0.2	0.1	0.5	0.3	0.8	0.9	19	0.2	0.4	0.2	0.05	0.01	0.04
MPC (maximum permissible concentration)		700.0			4.0			3.0			23.0			6.0			0.05		

Excess over MPC is highlighted with bold. AL—alluvial-meadow soil, L—meadow soil, AS—alluvial-stratified soil.

in the floodplain in the general direction of the NPS and is affected by waste products.

The amount of exchangeable Pb forms in station soils is 5–33% of the total content. The higher relative content of Pb^{2+} is linked with its ion radius. It is close to the ion radius of Ca^{2+}, which plays an important role in ion-exchange interactions (Minkina, 2008).

Exchangeable Cd forms, as well as their total content, exceed the MPC in the soils of many monitor stations (Table 2). The highest extractability of Cd by ammonium-acetate buffer has been confirmed in works of researchers (Plekhanova et al., 2001; Fateev et al., 2001; *Khimiya*..., 1985; etc.). The authors provide the share of Cd that transfers to this extract: it ranges from 22 to 60% of its total content.

By the content of exchangeable Mn forms, all of the studied grounds are not polluted (Table 2, Fig. 5), however, a 2.5- to 10-fold variation of the content of this metal is observed depending on soil properties (stations 1 and 2).

HMs in the studied soils form a series by the relative content of exchangeable forms (% of total amount): Cd > Pb ≥ Mn > Zn ≥ Ni > Cu.

The content of the studied HMs in complex forms is in most cases higher than in exchangeable ones (Table 2, Fig 5). HMs form a series by the content of complex forms in soils (% of total amount): Pb ≥ Cu > Mn > Zn > Ni > Cu.

The relative content of complex forms of Zn and Ni in the studied soils is only 1–12% of the total content, which is explained by the weak complex-formation ability of Zn and Nu with organic matter (Piccolo and Stevenson, 1982). However, the contribution of complex forms of Pb can reach one-third of the total metal content in the soil.

The highest content of mobile metal compounds is represented by their specifically sorbed forms, which makes a potential reserve of elements. In alluvial-meadow saturated soils, which form on carbonate sediments and have an alkalescent reaction in HM immobilization, the role of ferric and manganese hydroxides increases, as well as that for carbonates in the specific sorption of metals.

In the studied soils, the contents of specifically sorbed metal forms are ordered in the following sequence (% of total content): Mn ≥ Cu > Pb > Zn > Ni > Cd.

CONCLUSION

The informativeness of the approach used in this work, which was based on a ranking of metal compounds that are strongly or weakly bounded in the soil, was proven. The results allowed us to detect regional specific features in the formation of HM compounds in floodplain soils of the Don River estuarine region and the changes that occur with soil pollution and to detect the influence of different factors on the transformation of metal compounds in the soils and estimate them ecologically.

It was shown that the distribution of gross HM content in the investigated soils is determined primarily by their content in pedogenic species of the Don river floodplain, as well as by soil factors: the organic matter content and granulometric composition. The system of chemical element compounds forms a relationship of different compound groups, with strongly bound metal forms predominating. The soils can be ordered by their ability to strongly retain Cd, Pb, Mn, Zn, Cu, Ni: alluvial-meadow heavy-loam > alluvial meadow light-loam > meadow alluvial-deposited > alluvial-meadow sandy and sandy-loam > alluvial-stratified sandy. This series completely corresponds to the decrease in their HM buffering capacity.

Among weakly bound metal compounds, specifically sorbed forms predominate. At some monitor stations, pollution by exchangeable forms of copper, zinc, and cadmium was found, which suggests technogenic HM accumulation. On the whole, the regularities in the distribution of mobile HM forms in the soil reproduce the regularities established for the distribution of their gross content.

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