

## Exchangeable form of potentially toxic elements in floodplain soils along the river-marine systems of Southern Russia

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### Abstract

Large rivers and especially their deltaic parts and adjacent coastal zones are subjected to strong anthropogenic influence and are often considered as hotspots of environmental pollution. The Don River is one of the largest and most important rivers in the South of Russia. The Don River basin is a highly urbanized area with developed agriculture and industry which negatively affect water quality, aquatic ecosystems and soils. The main objectives of the proposed research were to determine the levels exchangeable form of PHEs in soils of various aquatic landscapes of the study area, as well as to reveal the relationships between the content of exchangeable PTEs and the physical-chemical properties of floodplain soils. The obtained results showed that soils of the Lower Don and Taganrog Bay coastal zone are rather contrast in terms of properties and metal contents, which indicates the variability of landscapes, natural and anthropogenic processes in the studied systems. High CV values for a number of metals such as Pb, Zn, Cd and Cr indirectly indicate strong anthropogenic influence on these environments. The group median values for extractable forms for most of the metals except for Cu and Ni were higher for urbanized areas. The results of PCA analysis showed that there are two association of metals in terms of geochemical behavior and sources. The first one included Cr-Zn-Pb-Cd, the elements of anthropogenic origin, the second Mn, Ni, and Cu, which are probably of mixed origin. The obtained results showed that the Lower Don and Taganrog Bay coastal zone is a diverse and complex system subjected to anthropogenic activities, which is pronounced in the enrichment of aquatic soils with a number of metals and higher proportions of exchangeable forms from different types of sources that likely can be of both local and whole basin scale.

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### Introduction

Deltas of large rivers and adjacent coastal areas are transitional environments, where parameters of the media and element mobility change significantly at rather short distances, and interactions between fluvial and marine processes significantly affect their geochemistry (Dada et al., 2016; Botsou et al., 2019). Chemical and physical gradients typical for such systems lead to the partial removal of both suspended and dissolved matter, which sequentially results in the formation of barrier zones (Chen et al., 2020; Savenko and Pokrovsky, 2020). The filtration capacity of river deltas is important for the protection of marine

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ecosystems, but the accumulation of pollutants in deltaic landscapes aggravates their degradation (Lychagin et al., 2015; Kasimov et al., 2020a,b; Chalov et al., 2020). Thus, delta geochemistry studies are very informative for tracking anthropogenic activities within the entire river basin, since various components of such systems provide information on both current and historic pollution (Beltrame et al., 2009; Loureiro et al., 2009; Uluturhan et al., 2011; Dhanakumar et al., 2015; Birch et al., 2015; Buscaroli et al., 2021).

River deltas and adjacent coastal zones are highly dynamic systems subject to seasonal and long-term fluctuations of stream runoff and fluxes of dissolved and suspended matter, storms or floods, as well as anthropogenic processes in basins (Kasimov et al., 2020a,b). Consequently, environmental management and pollution control for deltaic landscapes requires consideration of many factors, including the geomorphological structure and hydrology of a particular river mouth, land-use and erosion processes in the basin (Greening et al., 2014; Chapman and Darby, 2016; Ahn et al., 2020; Fulford et al., 2020). Moreover, efficient management of deltas is impossible without systematic geochemical monitoring of water, sediments, macrophytes and soils. The latter are of particular interest, since they are complex heterogeneous systems subject to flooding and redox fluctuations. It is important to note, that deltaic alluvial soils in highly urbanized regions are affected by strong anthropogenic pressure, which leads to their transformation due to agricultural or recreational activities, atmospheric and hydrogenic pollution (Arafa et al., 2015; Shokr et al., 2016; Thinh et al., 2018; Yan et al., 2018; Enya et al., 2019; Elbehiry et al., 2019; Ge et al., 2019; Hu et al., 2020; Lu et al., 2020).

The Don River is one of the most important rivers in European part of Russia. The entire Don basin has been greatly transformed as a result of long-term intensive anthropogenic load (Bartsev et al., 2016). Highly productive arable land in southern Russia, industrial and mining clusters, concentrated mainly in the watershed of the Seversky Donets tributary, and intensive development of the Rostov-on-Don agglomeration are the main factors that negatively affect the lower part of the Don basin (Nikanorov and Khoruzhaya, 2012; Matishov et al., 2016; Bauer et al., 2018; Konstantinova et al., 2020; Linnik et al., 2020; Minkina et al., 2020; Sushkova et al., 2020). The highest degree of anthropogenic load is characteristic of the Don Delta and the coastal zone of the Taganrog Bay due to urbanization, river and sea transport, as well as recreational activities, which leads to a decrease in water quality, soil and sediment pollution, degradation of coastal and deltaic landscapes and vegetation (Chichaeva et al., 2020).

Potentially toxic elements (PTEs) are one of the most dangerous pollutants for aquatic and subaqueous landscapes of the Lower Don and the Taganrog Bay (Nikanorov, 2014; Tkachenko et al., 2016, 2017). Previous geochemical studies within the Don Delta and the coastal zone of the Taganrog Bay revealed a strong variability in the PTEs content in soils and plants (Minkina et al., 2017a, b, 2019; Nevidomskaya et al., 2020). The main objectives of this study were (1) to determine the levels of total and exchangeable form of PTEs in soils of various aquatic landscapes of the study area, (2) to reveal the relationships between the content of exchangeable PTEs and the physical–chemical properties of floodplain soils.

## Material and Methods

### Study area and soil sampling

The floodplain soils, representing various zones of the Lower Don–Taganrog Bay system, have been analyzed in this study. Depending on the soil-landscape and hydrological conditions and taking into account the intensity of anthropogenic influence, the following zones were identified: the lower Don floodplain from the Tsimlyansk Reservoir to the source of the Mertvy Donets River, Don Delta, the coastal zone of the Taganrog Bay, the mouths of small rivers flowing into the bay, and Taganrog city, an industrial port center on the northern coast of the bay (Figure 1).

The valley of the Lower Don is characterized by the presence of wide floodplain develops with an abundance of above-water and meadow vegetation. The Don Delta is represented by several sandy islands, densely indented by gently sloping depressions of dried old riverbeds. Delta arms and ducts have natural riverbed shafts up to 1.5 m above low-water level (Korotaev and Chernov, 2018). The total area occupied by modern Don Delta is estimated at 540 km<sup>2</sup> (Ivanov et al., 2013). The northern shore of the coast of the Taganrog Bay is characterized by the predominance of abrasion and erosion processes, the southern part, from the Dolgaya Spit, is distinguished by relatively more intense accumulative processes (Krylenko et al., 2017). In addition to the Don River, floodplains of smaller rivers, that flow into the bay, such as the Kagalnik, Mius, Sukhaya Chuburka, and Mokraya Chuburka were also analyzed. The degree of the anthropogenic impact on coastal soils due to the urbanization was assessed on the example of the city of Taganrog.

The climate of the studied territory is moderately continental, the average annual temperature is 9.9 °C, and annual precipitation is 615 mm (Kazakov, 2020). In terms of hydrology and hydrochemistry, the Don estuary is complex system strongly controlled by surges up and down with frequent flows of marine water into the

delta branches, especially during periods of low water (Chikin et al., 2019). The chemical composition of the water varies from sulphate-calcium at the upper delta to chloride-sulphate-sodium at the seaside, mineralization varies from 300-500 mg L<sup>-1</sup> in the middle part of the river mouth to 1–2 g L<sup>-1</sup> near the sea, while the pH values fluctuate in a smaller range (7.5-8.5) (Tkachenko et al., 2016).

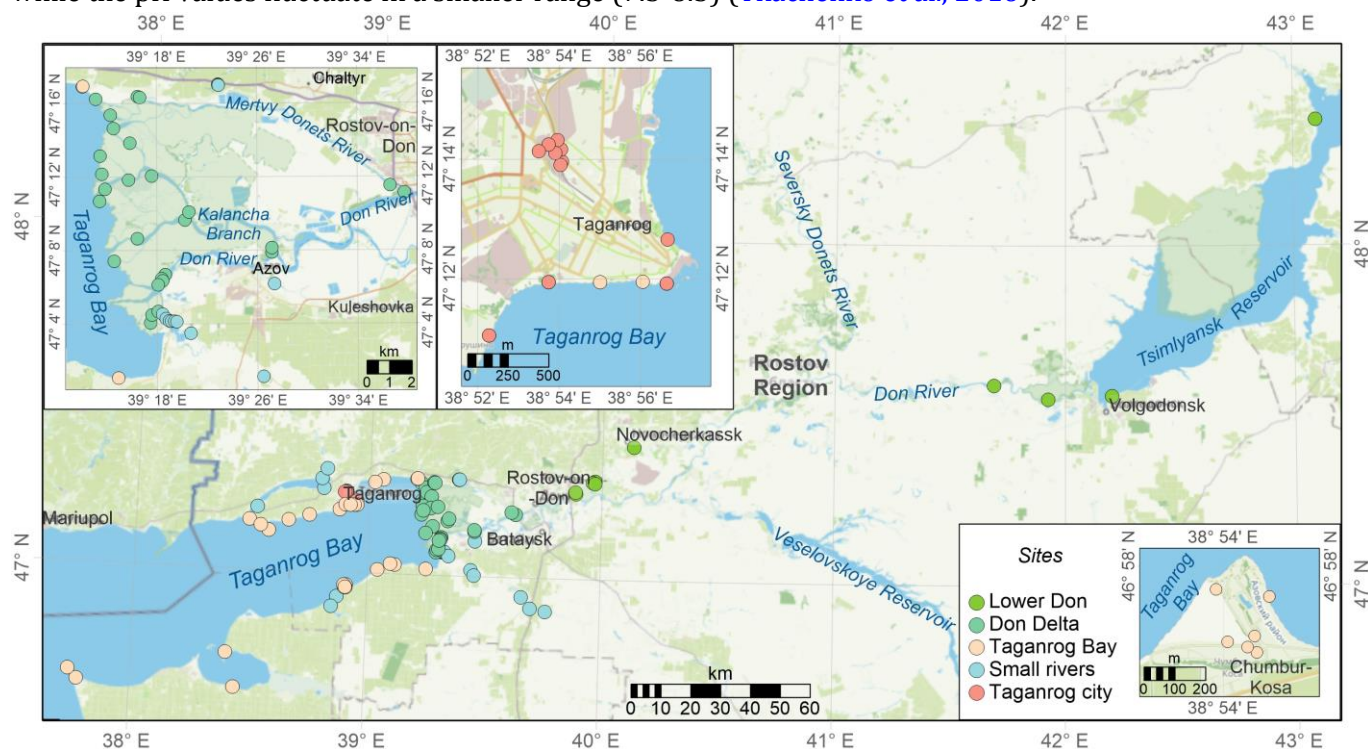


Figure 1. Simplified map of study area, showing various key sites and location of sampling points (basemap from [www.openstreetmap.org](http://www.openstreetmap.org)).

Floodplain and coastal landscapes of the Lower Don and Taganrog Bay are represented by alternation water bodies, coppice willows, floodplain meadows, sand dunes, beaches and spits, parks, gardens and other tree plantations. The most common macrophytes of the Lower Don and coastal zones of the Taganrog Bay belong to the families *Asteraceae*, *Poaceae*, *Fabaceae*, *Brassicaceae*, *Apiaceae*, *Lamiaceae*, and *Scrophulariaceae* (Kolomyichuk and Fedyaeva, 2012; Matishov et al., 2014). The floodplain and coastal landscapes of the study area are dominated by *Fluvisols* (according to IUSS, 2015), which differ significantly in texture, salinity, and organic matter content. *Fluvisols* are formed on medium and fine alluvial sands and sandy loams, characterized by a stratification of the profile and underdeveloped genetic due to periodic flooding and redeposition of particles (Minkina et al., 2017a,b). *Solonchaks*, *Arenosols* and *Haplic Chernozems* which are background soils of the region are less common.

Soil samples were collected in summer 2020 using an envelope method (GOST 17.4.4.02-2017, 2018) from the surface soil horizon (0–20 cm deep). The soil samples were air-dried, mixed, ground, and passed through a 1-mm sieve (Vorobyova, 2006).

### Physical and chemical analyses

The particle size analysis was conducted using the pipette method to obtain the clay fraction (<0.001 mm) and physical clay fraction (<0.01 mm). The total organic carbon (TOC) content in the soils was determined using the dichromate oxidation method according to Tyurin. The pH was measured by potentiometry in the supernatant suspension of soil and water in a ratio of 1:2.5. The CaCO<sub>3</sub> content was determined by the complexometric method proposed by Kudrin (Vorobyova, 2006). The exchangeable cations Ca<sup>2+</sup> and Mg<sup>2+</sup> were determined using the method described by Shaimukhametov (1993).

The total concentrations of Cr, Mn, Ni, Cu, Zn, Cd, and Pb were determined by X-ray fluorescence analysis using a Spectroscan MAX-GV spectrometer (Spectron, Russia) (OST 10-259-2000, 2001), and the content of exchangeable forms extracted from the soil by NH<sub>4</sub>Ac buffer solution with pH 4.8 and soil/solution ratio of 1:10 for 18 h was determined by atomic absorption spectrophotometry (AAS) (KVANT 2-AT, Kortec Ltd, Russia) (RD 52.18.289-90, 1990). All laboratory tests were performed in triplicate. The accuracy of element determination was verified using duplicates, reagent blanks, and state standard reference samples (no. GSS 10412-2014, State Service for Standard Specimens Relating to Composition and Properties of Substances and Materials) and complies with standards of certified methods (RD 52.18.289-90, 1990; OST 10-259-2000, 2001).

## Statistical analysis

Descriptive statistics of PHEs concentrations and soil properties, including mean, median maximum, minimum values, standard deviation (SD), and coefficients of variation (CV) were calculated. The Kolmogorov–Smirnov test with Lilliefors correction disposed the normal distribution of all data; therefore, raw data was standardized by means of z-score before multivariate statistical analysis.

To analyze the significant differences in exchangeable PTE content in the soils of various zones of the Lower Don–Taganrog Bay system, one-way analysis of variance (ANOVA) and Fisher LSD. Pearson correlation coefficients ( $r$ ) were calculated to determine the relationship between exchangeable PTEs and physical–chemical properties of soils. Principal component analysis (PCA) was carried out in order to identify relationship between the measured parameters by achieving individual component loadings. Only components with eigenvalues above 1.0 were considered, following the Kaiser criteria. All of these analyses were performed using STATISTICA 12 (Statsoft, USA), and statistical significance was determined at  $p < 0.05$ .

## Results and Discussion

### Soil physical–chemical properties

The descriptive statistics for physical–chemical properties of soils of the Lower Don and Taganrog Bay coastal zone are present in Table 1. One can see that most of the studied parameters varied significantly. The  $\text{CaCO}_3$  content varied from 0.1 to 8.3 %, the TOC content – from 0.1 to 3.9 %,  $\text{Ca}^{2+}$  and  $\text{Mg}^{2+}$  3.2 to 36.3 and from 0.2 to 8.3  $\text{cmol}_c \text{ kg}^{-1}$  respectively and the clay from 0.1 to 33.1 %. The differences in the content of  $\text{SiO}_2$ ,  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  correspond to the variations of soil texture with maximum  $\text{SiO}_2$  values characteristic for soils of sandy beaches and higher proportion of  $\text{Fe}_2\text{O}_3$  and  $\text{Al}_2\text{O}_3$  is characteristic for well-developed accumulative *Fluvisols* with higher contents of clay fraction. The values of the CV are rather high for  $\text{CaCO}_3$  (78.4%), TOC (61.5%),  $\text{Ca}^{2+}$  (50.4%),  $\text{Mg}^{2+}$  (66.9%), and clay fraction (70.0%). High heterogeneity of soil properties indicates the diversity of landscapes and parent material within the large river system and coastal environment. Studied soils develop whin various geomorphic forms that may differ significantly in hydrological regime, current sedimentation processed and, in general, by their timing of pedogenic processes. All studied soils were alkaline, from slightly to strongly. At the same time pH values showed smaller variation (CV=4.1%), which can be explained by the fact that all studied soils appear in semi-arid climatic condition and carbonate-reach loess is the most common type of covering deposits within the Lower Don basin.

Table 1. Descriptive statistics for physical–chemical properties of soils of the Lower Don and Taganrog Bay coastal zone (N=97)

Statistics*	pH H <sub>2</sub> O	CaCO <sub>3</sub>	TOC	Ca <sup>2+</sup>	Mg <sup>2+</sup>	SiO <sub>2</sub>	Fe <sub>2</sub> O <sub>3</sub>	Al <sub>2</sub> O <sub>3</sub>	Clay	Physical clay
										%
Mean	7.9	2.4	1.3	16.1	2.7	63.8	3.6	8.1	14.1	29.7
Median	7.9	1.9	1.1	16.0	2.0	63.8	3.9	8.5	12.2	26.4
Minimum	7.2	0.1	0.1	3.2	0.2	37.0	0.4	1.2	0.1	1.3
Maximum	8.9	8.3	3.9	36.3	8.3	85.2	6.7	11.8	33.1	67.8
SD	0.3	1.9	0.8	8.1	1.8	9.9	1.3	2.6	9.8	17.3
CV	4.1	78.4	61.5	50.4	66.9	15.5	36.1	32.3	70.0	58.4

\* TOC total organic carbon content, SD standard deviation, CV coefficient of variance.

### Levels of PTEs in the studied area

The data on the concentrations of total and exchangeable forms of metals is summarized in Table 2. Based on the descriptive statistics it is possible to conclude, that total concentrations of all PHEs showed significantly variability in soils of the Lower Don and Taganrog Bay coastal zone. The studied PHEs can be subdivided in two groups based on the values of CV. The first group includes Mn (47.2%), Ni (38.1%) and Cu (46.2%), and the second group includes Cr (84%), Zn (116.8%), Cd (111.7%) and Pb (101.3%). High CVs are characteristic of the second group, and confirm the heterogeneity of PHEs. The fact that the CV for the second group of elements is 2–3 times higher than for the first indicates that they are better indicators of anthropogenic activities and pollution in soils of the studied aquatic system. This is consistent with the data on the exchangeable forms of PHEs. In general, we can mention that the CV values for exchangeable forms of all studied metals were higher than for total concentration, especially for Zn (182.0) and Pb (175.5). It can be explained as consequence of anthropogenic impact on the Lower Don basin, as well as Zn and Pb are good indicators of anthropogenic activity. It should be noted that studied soils are rather different in terms of carbonate, organic carbon and clay content, which strongly affect their sorption properties and geochemical status.



Table 2. Descriptive statistics for PTEs (mg kg<sup>-1</sup>) in soils of the studied area (N=97)

Concentration	Element	Mean	Median	Minimum	Maximum	SD	CV
Total	Cr	109.2	94.9	34.1	871.0	91.7	84.0
	Mn	861.6	729.3	110.3	2466.2	406.6	47.2
	Ni	46.5	45.3	19.0	98.0	17.7	38.1
	Cu	43.9	40.5	4.1	143.4	20.3	46.2
	Zn	147.9	94.3	19.4	1389.7	172.7	116.8
	Cd	1.7	0.9	0.1	10.0	1.9	111.7
	Pb	47.5	33.0	5.3	317.0	48.1	101.3
Exchangeable	Cr	3.8	2.8	0.3	62.6	6.6	173.7
	Mn	80.9	65.2	7.7	363.0	61.1	75.5
	Ni	2.5	1.9	0.6	8.5	1.8	70.7
	Cu	2.6	1.7	0.2	23.3	3.4	130.0
	Zn	20.5	7.0	1.3	295.5	37.3	182.0
	Cd	0.14	0.08	0.01	0.90	0.16	116.0
	Pb	4.8	2.7	0.2	60.4	8.3	175.5
Exchangeable percentage	Cr	3.0	3.0	0.6	7.2	1.4	46.7
	Mn	8.7	7.9	4.2	14.7	2.8	32.6
	Ni	5.3	5.3	1.5	10.1	2.2	40.9
	Cu	5.3	4.6	0.6	21.8	3.9	72.4
	Zn	10.0	8.5	1.5	21.3	5.0	50.4
	Cd	8.5	8.3	2.3	20.0	4.1	47.6
	Pb	8.3	8.0	2.6	19.1	3.5	42.3

The Figure 2 illustrates variability of the exchangeable PTE content in soils of the studied area. The highest level of variability for Pb, Cr and Zn were observed for soils from Taganrog. Soils of small rivers showed significant variability of Mn, Cu and Ni. For exchangeable Cd, the greatest variability was observed in the Don Delta soils, which can be interpreted as an evidence of geochemical barrier, related to the changes in pH values. According to the Wilks lambda criterion, the confinement of soils to a specific zone of the river-marine system is highly significant for all studied PHEs ( $p < 0.0005$ ).

Significant differences in exchangeable PHE content for different zones were observed: highly significant for Zn and Pb, strongly significant for Cd, and statistically significant for Cr and Cu (Table 3). In the urban soils of Taganrog, an excess of the average level of exchangeable Cr, Zn, Cd, and Pb was shown (Figure 2), which indicate the anthropogenic origin of these PHEs in the soils of the territory under consideration.

Table 3. Effects of the soil location within the Lower Don–Taganrog Bay system on exchangeable PTEs content as indicated by one-way ANOVA

Exchangeable metals	Sum of squares (SS)	Mean square (MS)	F	p
Cr	12.248	3.062	3.363	0.0129*
Mn	6.395	1.599	1.642	0.1705
Ni	8.187	2.047	2.144	0.0816
Cu	11.766	2.941	3.213	0.0162*
Zn	33.716	8.429	12.450	0.0000*
Cd	14.825	3.706	4.201	0.0036*
Pb	35.415	8.854	13.444	0.0000*

\* significant at  $p < 0.05$ .

The soils of small rivers were characterized by increased values of exchangeable Cu, the content of which was 2 times higher than in the soils of other zones. Copper exhibits organophilic properties in soils (Kabata-Pendias, 2011); its accumulation can be associated with more pronounced processes of humus accumulation, since the soils small river floodplains are enriched with organic matter transported from local arable land due to the erosional processes.

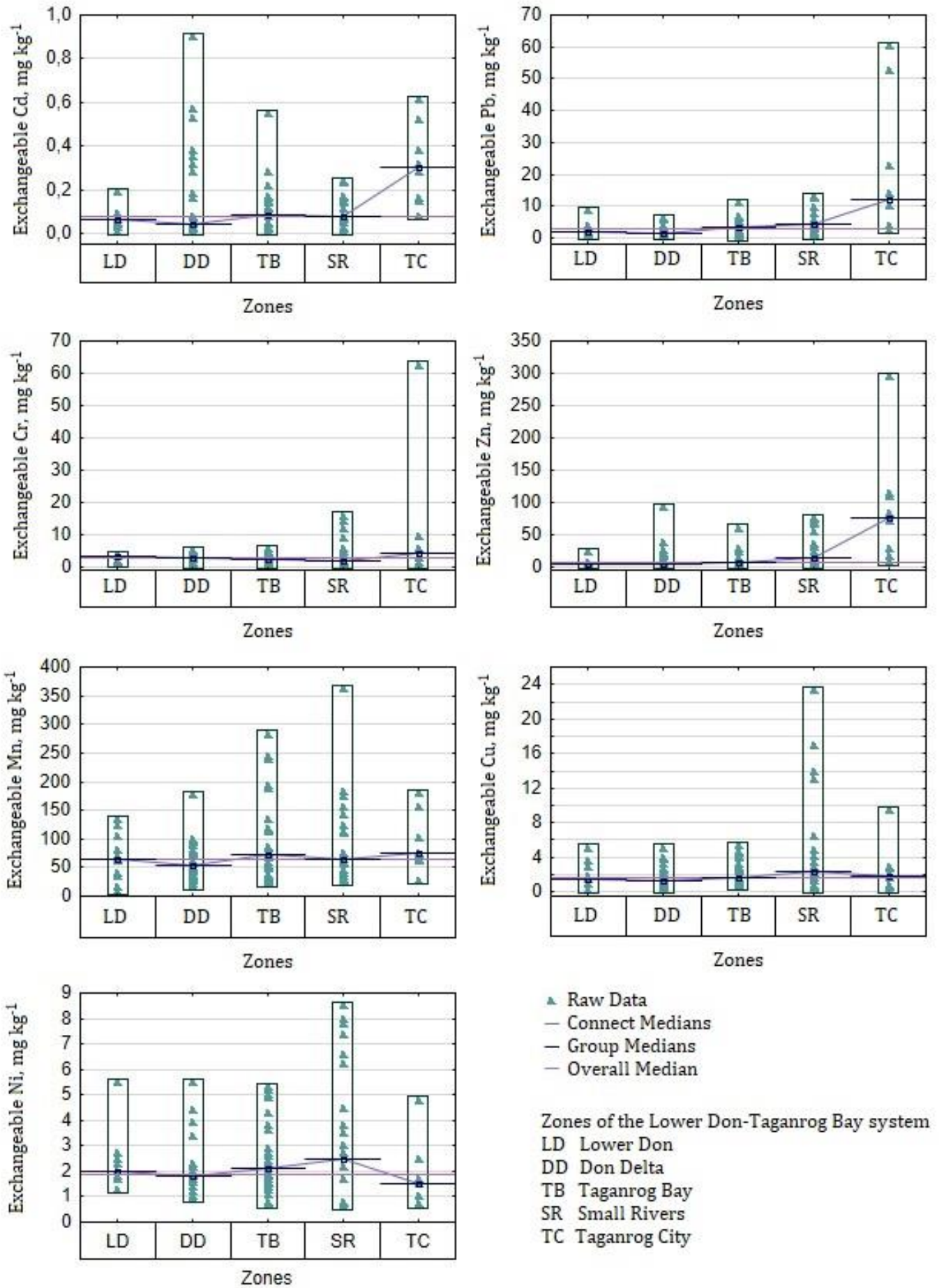


Figure 2. Variability plots of the exchangeable PTE content in soils within the study area.

### Relationship between soil properties and exchangeable PTEs content

The results of correlation analysis showed that soil properties have weak effect on the accumulation of exchangeable PTEs (Table 4). Statistically significant ( $p < 0.05$ ) low negative correlations were observed between physical clay and Ni, SiO<sub>2</sub> and Zn and Pb, as well as low positive correlations were observed between Fe<sub>2</sub>O<sub>3</sub> and Zn and Pb, Mg<sup>2+</sup> and Pb. Moderate correlations were found only between Mn and SiO<sub>2</sub>. The data obtained indicate the absence of a linear relationship between the studied parameters.

Table 4. Pearson correlations between exchangeable PTE content and soils properties

N=97	Cr	Mn	Ni	Cu	Zn	Cd	Pb
pH	0.136	0.044	-0.108	0.011	0.181	0.167	0.182
CaCO <sub>3</sub>	0.192	-0.045	-0.118	0.005	0.300*	0.043	0.244*
TOC	-0.046	0.018	-0.222*	-0.151	0.179	0.153	0.223*
Ca <sup>2+</sup>	-0.036	-0.048	-0.276*	-0.209*	0.113	0.004	0.163
Mg <sup>2+</sup>	0.099	-0.004	-0.183	-0.070	0.246*	0.147	0.319*
SiO <sub>2</sub>	-0.174	-0.569*	-0.117	-0.243*	-0.339*	-0.201*	-0.331*
Fe <sub>2</sub> O <sub>3</sub>	0.274*	0.127	0.133	0.078	0.339*	0.230*	0.317*
Al <sub>2</sub> O <sub>3</sub>	0.155	0.051	0.125	0.041	0.183	0.081	0.131
Clay	-0.035	-0.106	-0.299*	-0.202*	0.134	0.055	0.197
Physical clay	-0.014	-0.081	-0.307*	-0.191	0.161	0.122	0.223*

\* significant at  $p < 0.05$ .

Two principal components (PC) were identified, accounting for 67% of the total variance (Figure 3). Exchangeable forms of PTEs with high factor loadings were distributed among the factors as follows. The first PC characterized by the Cr-Zn-Pb association had the most significant strong negative value. The same factor had a moderate negative loading for Ni, Cu, and Cd. Moderate positive loadings for Mn, Ni, and Cu were characterized by PC2. The first PC also weakly correlates with content of Fe<sub>2</sub>O<sub>3</sub> (-0.333) and SiO<sub>2</sub> (0.388). Fractions of clay and physical clay showed weakly negative effects on PC2. Other soil properties were not associated with either PC1 or PC2. For each sampling site, factor loadings were calculated, which were projected onto the plane of PC1 and PC2. The first PC has the greatest influence on urban soils, while the PC2 manifests itself most strongly in relation to the soils of small rivers. Thus, it can be assumed that the PC1 is associated with anthropogenic impact, and the PC2 is associated with the natural processes.

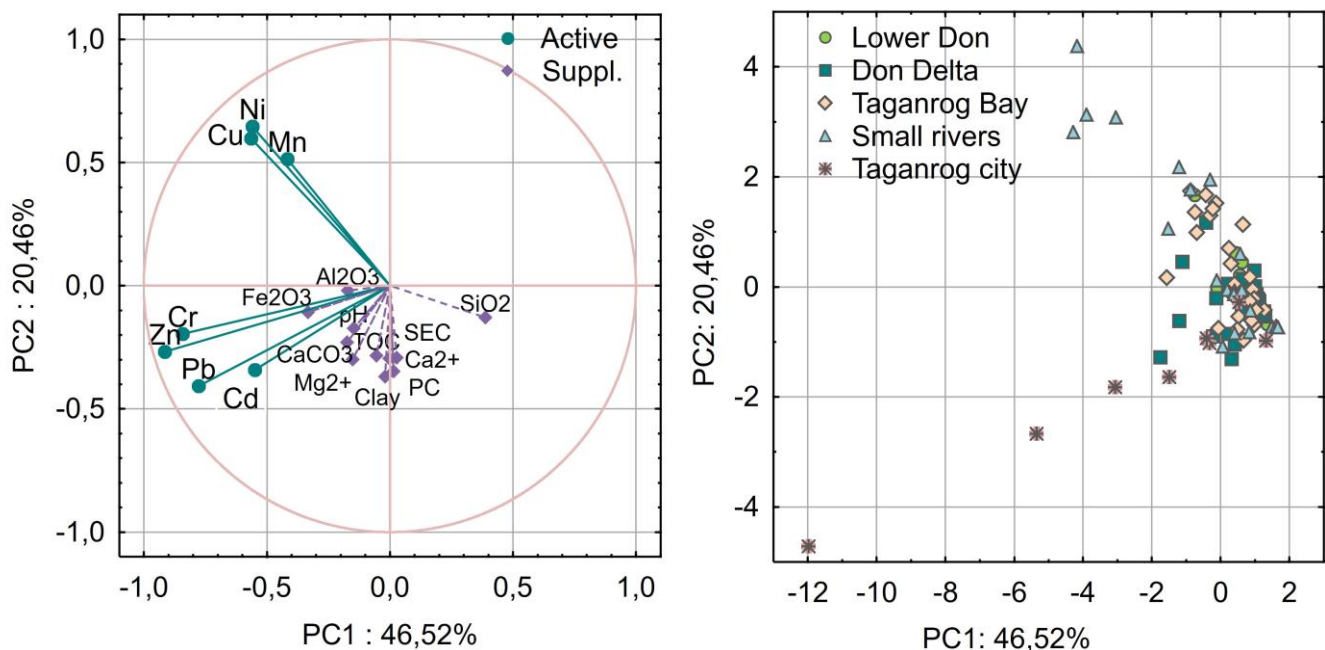


Figure 3. Plots of factor loadings revealed from principal component analysis, indicating the relationships between exchangeable PTE content and soil properties (left), and reflecting the degree of influence of factors on exchangeable PTE content in the soils of sampling sites (right).

## Conclusion

The study results have shown that the Lower Don and Taganrog Bay coastal zone is a complex system with a wide diversity of environments. This thesis is supported by the data on the properties of soils, representing different landscapes of the study areas. It was shown that most of the studied metals, especially Pb, Zn, Cd and Cr, have showed high CV values for both total concentrations and their exchangeable forms. This fact supported by the results of PCA analysis can be interpreted as signs of strong anthropogenic influence on this aquatic system. The obtained results showed that different parts the Lower Don and Taganrog Bay coastal zone are rather contrast in terms of soils, their properties and the degree of anthropogenic impact, which is manifested in significant variance of metals exchangeable forms and their proportions. Thus, the studies on the soil-geochemical features of the studied aquatic environments require complex investigation of mechanisms responsible for the geochemical behavior of potentially toxic elements.

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