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Potentially toxic elements (PTE) in soils on the megaprofile Eastern Donbass – Azov sea

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Abstract. An expedition was carried out to take soil samples of Eastern Donbass and other districts of the Rostov region. The main goal was to study the distribution of potentially toxic elements (PTE) in soils. The total content of mineral components in solid-phase samples was determined by using the X-ray fluorescence method. It was found that, according to the average concentrations, PTE`s line up in the following series: Fe>Mn>Zn>Cr>V>Cu>Ni>Pb>Co. The contents of Zn and Cu in the soil were compared by seasons. It was determined that PTE concentrations in the upper layer of soils were higher in winter than in summer. Geochemical spectra were constructed. They demonstrated that the concentration Clarks of Cr, Cu, Zn, Co, Pb exceeded the Clarks of these elements in the Earth's crust. Against this background, Pb stands out with contrast, the concentration in the soil of which exceeds those in the earth's crust by 2.8 times. The tightness of the relationship between the content of PTE in soil samples was calculated, which turned out to be a high straight line.

1 Introduction

Not only extensive geomorphological, tectonic, and lithological conditions, but also technogenic disturbances affect the territory on which the megaprofile "Eastern Donbass - Sea of Azov" is laid. Soils throughout the megaprofile were represented by ordinary carbonate chernozems [1, 2]. When moving along the megaprofile in the south-westerly direction, the thickness of the sedimentary cover of deposits of Quaternary and Neogene age, represented by loams, clays and limestones, increases. They cover the rocks of the Paleogene, which are manifested in the coastal sediments of some areas. Carboniferous rocks in the southern direction are submerged under Neogene and Quaternary deposits. In general, the studied territory is represented by flat spaces that are gently inclined towards river valleys and are strongly dissected by a ravine-girder network [3]. The territory of Eastern Donbass within the Rostov region is characterized by the highest density of mining enterprises. Both coal mines and quarries for the extraction of refractory and refractory clays, clays for brick raw materials, clay shales, sandstones are concentrated here [4]. One of the oldest coal-mining regions of Russia, the Donetsk Coal Basin, is located in the Eastern Donbass. The presence of coal rock terricons is a characteristic feature of the

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landscape of the open part of the Eastern Donbass. They, like the dumps, are composed of carbonaceous mudstones, siltstones, crushed sandstones. There are everywhere quarries passed for the extraction of various construction minerals. When moving along the megaprofile in the southern direction, the presence of numerous industrial and urban agglomerations becomes an absolute technogenic dominant [5]. Geomorphologically, the open Eastern Donbass is an elevated plain dissected by gullies and ravines. The beams cutting through this plain have a canyon-like structure, deluvial cover on their slopes, and sometimes on the bottoms of the beams, as a rule, is absent, and the bedrock comes to the day surface [3].

In accordance with the proposed temporary geological and industrial classification [6], the association of harmful impurities in the coals of the Donetsk basin includes the following elements: Hg, As, Be, Zn, Mn, V, Cr, Ni, Co, Pb, Cd. The analysis of the specifics of mining and the characteristics of the metalliferous coal of Eastern Donbass allowed L.Ya. Kizilstein [7] to identify a complex of potentially dangerous chemical elements for the environment to be taken into account when conducting lithochemical testing of soils and necessary for monitoring ecological-geochemical and sanitary-hygienic assessment of industrial sites of mines and rock dumps of Eastern Donbass (in order of decreasing the hazard class): Hg>Pb>Cd>Zn>Cr>Ni>Cu. In the works [1, 5], the granulometric and material composition of soils, road dust, bottom sediments of watercourses and reservoirs of Eastern Donbass and other districts of the Rostov region were studied in the summer, in which only two elements were identified - zinc and copper. The present study was carried out in winter and covers a wider range of trace elements.

2 Materials and methods

Since it is known that soils are one of the main sources of dust, including road dust, it is of scientific and practical interest to study the distribution of PTE in them. For this purpose, we have carried out expeditionary work in coal and predominantly urbanized areas of the Rostov region.

During the winter period of the expedition in 2022, soil samples were taken according to the megaprofile "Eastern Donbass –Azov Sea", which originates from the city of Shakhty, and ends in the village of Margaritovo. Its length was more than 150 km (Fig.1). It should be noted that in 2021 a summer expedition was conducted, which is described in detail in the work [1]. During this period, soil samples were taken at stations, including those located near the spoil tip and on top of its body, while in winter – near the roadway. At all stations, soil sampling was carried out in threefold repetition. Sampling, transportation, and storage of soil samples were carried out in accordance with the requirements of GOST 17.4.4.02-84 and GOST 12071-84, soil samples were taken using a plastic shovel in a layer of 0-5 cm. Samples of solid-phase material for chemical analysis were dried to an air-dry state according to GOST 5180-84. In the laboratory, the samples were freed from inclusions – plant roots, insects, stones. Then the soil was ground in a mortar with a pestle and sifted through a sieve with a hole diameter of 1 mm. Before determining the total content of mineral components, the sample was ground in an agate mortar to a powder state. The content of PTE, such as Ni, Cu, Pb, Zn, Cr, Fe, V, Mn, as well as other trace elements in solid-phase samples were carried out using the X-ray fluorescence method on the spectrometer "Spectroscan MAX- GV. The accuracy of the determination is up to 10% [8].

Fig. 1. Location map of sampling stations along the route "Shakhty - Margaritovo"

We calculated the coefficients proposed by V. I. Vernadsky to describe the differences in the content of chemical elements in a natural system or part of it from the Clark lithosphere. The Clark concentration (CC) is the ratio of the average content of a given element in a natural object (Ci) to the Clark of the lithosphere (K): CC = Ci / K. The Clark concentration allows us to judge the degree of concentration (CC > 1) or scattering (CC < 1) of a chemical element in the studied object relative to the lithosphere. In the case when the content of a chemical element is significantly less than the Clark of the lithosphere, the inverse of the Clark of the concentration is calculated – the Clark of scattering (CS). This coefficient shows how many times the concentration of an element exceeds its content in the studied natural object: CS = K/ Si. Thus, KK and CS allow us to estimate the concentration or scattering processes of chemical elements in the studied objects (rocks, soils, etc.) relative to individual parts of the lithosphere [9]. Clarks of chemical elements in the lithosphere according to A.P. Vinogradov (1962) were used for our calculation.

3 Results and discussion

Consider the distribution of PTE in the soil according to the profile "Shakhty – Margaritovo". The maximum value for Fe was 30940 mg/kg, the minimum value was 15190 mg/kg, the average for the profile was 22251.25 mg/kg. For Mn, the maximum is 1347.9 mg/kg, the minimum content is 327.7 mg/kg, the average (578.5 mg/kg). The maximum and minimum Pb values are 57.96 mg/kg and 9.91 mg/kg, respectively, the average is 38.3 mg/kg. For Ni, the maximum value is 67.82 mg/kg, the minimum is 24.05 mg/kg, the average is 42.73 mg/kg. The maximum value for Co is (38.77 mg/kg), the minimum is (9.23 mg/kg), the average for the profile is 19.4 mg/kg. For Cu, the maximum is 75.9 mg/kg, the minimum is 38.12 mg/kg, the average is 57.6925 mg/kg. The maximum and minimum values for Zn are (117.95 mg/kg) and (73.19 mg/kg), respectively, the average (100.5 mg/kg). For Cr, the maximum value is (106.44 mg/kg), the minimum is

(50.84 mg/kg), the average is (86.02625 mg/kg). The maximum for V is 93.58 mg/kg, the minimum is 30.51 mg/kg, the average is 61.8 mg.

Data analysis showed the following distribution of the average contents of PTE in the samples: **Fe>Mn>Zn>Cr>V>Cu>Ni>Pb>Co**. Earlier in the work [10], the distribution of some of these elements in soils in winter was analyzed, it is characterized by a slightly different change in the average concentrations of HM for a number of Zn>Cr>Pb>Cu>Ni, as well as other trace elements - Mn >V.

According to the hazard classes proposed in the work [7], we have identified the most toxic elements. The level of their toxicity varies in the range **Pb>Zn>Cr>Ni>Cu**. A trend in the growth of PTE content in the soils of the open Donbass was found. This is especially noticeable on the example of Fe, Mn, Ni and Co (Fig. 2). With the exception of 1 and 2 stations, there is a trend in Co. Another station where large amounts of PTE have been observed is Station 2a.

Compare the data of summer and winter expeditions on the content of Zn and Cu in the upper soil layer of the studied area. If in summer the concentrations of zinc and copper averaged 61.2 and 51.4 mg/kg [1], then in winter these values increased to 98.8 and 58.8 mg/kg, respectively. Such seasonal differences in PTE concentrations seem to be related to the fact that in winter, unlike in summer, the amount of their emissions into the atmosphere increases due to an increase in the volume of coal and other organic fuels burned. A similar phenomenon was described by the example of the content of one of the most harmful PTE - mercury, which increased in the precipitation of Rostov-on-Don and satellite cities during the heating season for a relatively warm period of time. According to [13], this was due to a sharp increase in the volume of dust and gas emissions generated by the combustion of coal, fuel oil and gas during the cold season. As an argument, they point out that the coals contain mercury in elevated concentrations compared to the host rocks of the Donetsk basin [7]. V.V.Privalenko, O.S..Bezuglova (2003) drew attention to the fact that the content of Cu and Zn in dust in winter precipitation in Rostov-on-Don is higher than in summer. In accordance with our proposed model the dust cycle [1] between anthropogenic and natural landscapes has reason to assume that the upper layer of soil involved in this process, especially roadside, in winter can be enriched to a greater extent with PTE, compared with summer.

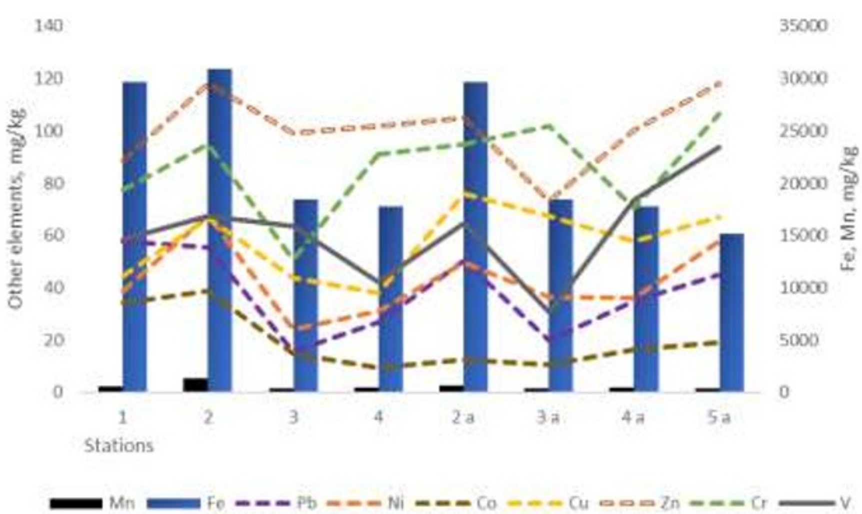

Fig. 2. Distribution of potentially chemical elements in soils according to the megaprofile "Shakhty – Margaritovo"

It was important to know not only the levels of PTE, but also the enrichment or depletion relative to the Clarks of chemical elements in the Earth's crust [11, 12]. To construct the diagram, calculations of the Clark concentration (CC) and Clark scattering (CS) were performed (Fig.3). Note that a number of elements Sg, Cu, Zn, Co, Pb exceeded the Clark of chemical elements in the Earth's crust. Pb is particularly distinguished, the concentration in the soil of which exceeds those in the earth's crust by 2.8 times. The content of trace elements such as Fe, Mn, Ni, V in the soil was lower than in the Earth's crust.

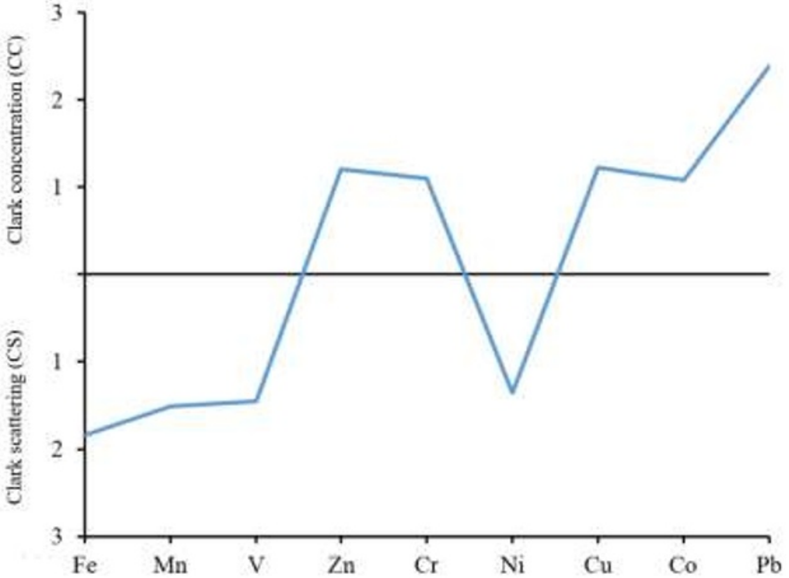

Fig.3 Geochemical spectra of PTE in soils

The closeness of the relationship between the amount of PTE in soil samples was calculated. Close - high direct connections were observed between Fe and Mn, Mn and Co, Cr and Cu, Cu and V, Ni and Pb, Pb and Co (Table). The presence of a connection between the content of these elements in the samples allows us to make an assumption about the unity of their origin.

Table. Correlation matrix between PTE in the soil

	Fe	Mn	Zn	Cr	Cu	Ni	Pb	Co	V
Fe	1								
Mn	0.77	1							
Zn	-0.40	0.13	1						
Cr	-0.01	-0.10	0.17	1					
Cu	0.08	0.20	0.2	0.73	1				
Ni	0.24	0.52	0.63	0.56	0.69	1			
Pb	0.29	0.31	0.44	0.42	0.34	0.73	1		
Co	0.61	0.73	0.31	-0.15	0.03	0.57	0.73	1	
V	-0.04	0.09	0.31	0.33	0.72	0.65	0.44	0.25	1

4 Conclusion

The article discusses the results obtained during the performance of expeditionary work on soil sampling in the epicenter of Eastern Donbass and outside the direct influence of coal mining areas of the Rostov agglomeration (Taganrog Bay area). Variations of PTE in soils according to the megaprofile "Eastern Donbass –Azov Sea" are calculated. It was found that the contents of PTE are located in the selected samples in the following sequence: **Fe>Mn>Zn>Cr>V>Cu>Ni>Pb>Co**. From this list, the most toxic elements are highlighted: **Pb>Zn>Cr>Ni>Cu**, which are characteristic of coal areas and urbanized areas of the Rostov region. Accumulation of Fe, Mn, Ni and Co was found in the northern part of the megaprofile. The average contents of Zn and Cu exceeded the values obtained during the summer expedition. This is because in winter, unlike in summer, the volume of their emissions into the atmosphere increases due to an increase in the amount of coal and other types of organic fuels burned. Consequently, by participating in the dust cycle, the upper layer of soil, especially roadside, can be enriched with PET to a greater extent in winter compared to summer. The Clarks of concentrations of elements such as Sg, Cu, Zn, Co, Pb and especially the latter exceeded the Clarks of these elements in the Earth's crust. The correlation between the content of several elements in soil samples turned out to be high and direct.

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