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ENVIRONMENTAL GEOCHEMICAL ASSESSMENT OF TECHNOGENIC SOILS

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The purpose of this study was to obtain diagnostic features and criteria for the distribution of heavy metals in technogenically altered soils in the area of industrial facilities, depending on their altered geochemical properties, which make it possible to fix chemical elements in landscapes (the formation of geochemical barriers). On the basis of the geoecological assessment, disturbance of the soil buffer properties, which is reflected in the ionic composition change, alkalization, pH increase, and sulfate-chloride salinization have been revealed. This forms the heavy metals alkaline barrier. For example, in case of Cu, Pb, Zn, and N, it contributes to their accumulation and subsequent concentration in the soil layer due to the exchange interactions between chemical elements and Na^+, K^+, Ca^{2+} cations. Soil saturation with sulphates also increases the probability of metals demobilization in the soil layer. It has been shown that intra-sectional soil migration of oil products (one of the most common pollutants of industrial areas) and chemical elements occurs at a depth of 30-50 cm, where the oil products based on a clay sorption layer form a technogenic barrier. The direct correlation between the oil content in the soil and the amount of toxic sulphate and chloride salts was found. The set of identified factors forms technogenic geochemical barriers in the industrial production area, on which pollutants and chemical elements, including heavy metals, are demobilized. The revealed effects are the rationale for creating artificial geochemical barriers on the migration path of both pollutants and valuable components with the aim of their subsequent extraction from the soil when developing an appropriate extraction method.

***Key words*:** heavy metals; geochemical barrier; geoecological assessment; migration

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Introduction. Exploitation of subsoil resources is characterized by the uncontrolled significant input of lost and non-reproducible valuable chemical elements into the soil horizons. More than 100 billion tons of ore is extracted from the Earth's interior, more than 400 million tons of minerals are dispersed on the surface, and geotechnologies are considered as a fundamental mining complexes impact on the environment objects, particularly, on the soils [9]. Man-made impact on the territory during and after the field mining consists in the mine, sludge, and tailings dump, solid and liquid wastes of different chemical composition [5]. Various substances enter the environment from technogenic formations and migrate within natural landscapes. As a result, technogenic fields and pollution halos can form in limited areas. Criteria for the state of technogenically altered geosystems are poorly studied, which does not allow us to estimate the scale of negative consequences.

A large number of works are devoted to the negative impact minimization on the environment, the issues of disturbed lands recultivation, and mining wastes utilization [10, 14, 16]. The authors show a scientific interest in ecological and geochemical research, regardless of the ore type, arguing that the scale of technogenic impact on the territory and the need to develop a diagnostic system of the environmental objects state in the context of increasing technogenesis. Currently, scientists are in search of effective methodological approaches for a comprehensive geoecological assessment of disturbed areas. The systems for ecological and geochemical monitoring are also created during the natural resources development [4, 7, 11]. In recent years, the focus of geo-environmental research has changed. A lot of scientific schools are focused on the study of the geochemical patterns of substance distribution in the upper lithosphere and soil, as well as the systematization and generalization of causes governing the mobility of chemical elements [2, 3, 6].

In order to understand the mechanisms of substance migration in the technogenic conditions, it is necessary to determine the criteria and quantitative dependences of the chemical elements and pollutants behavior, as well as to find the relationship between geochemical parameters and altered characteristics of the soil medium [8, 12, 13, 15]. This allows identifying geochemical barriers in the migration way of both pollutants and valuable components in order to extract them.

Problem statement. Actual problems of geochemistry of technogenically altered landscapes are the study of chemical elements migration patterns, the identification of their lateral and intra-profile distribution, obtaining evidence of their fixation depending on environmental conditions. At the moment, more than 200 ore types are mined, but the real losses of valuable chemical elements scattered on the surface have not yet been taken into account. The soil is a powerful natural barrier that can accumulate chemical elements, removing them from the biogeochemical elements circulation. Therefore, the problem of chemical elements and substances behavior in technologically modified soils is very relevant.

The purpose of this study was to obtain diagnostic features for the heavy metals (HM) distribution in technogenically altered soils depending on their geochemical features, which make it possible to fix chemical elements.

Research problem:

1. Determination of the criteria for disturbance of the soil buffer properties on the basis of key indicators of the state, as well as the salinization of the technogenic impact area.

2. Obtaining empirical dependencies that reveal the possibility of geochemical barriers on the HM migration way within the technogenic impact area.

3. Analysis of the relationship between the HM distribution in the soil and the content of petroleum products (PP), considered as the most common pollutants.

Methodology. The research methodology was based on the theoretical foundations of landscape geochemistry and the concept of technogenic geochemical barriers [3, 6]. We believe that the study of the elements migration flows in soils contributes to the identification of the potential artificial barriers in the limited area. In the future, this will allow creating «secondary mineral deposits» with the possibility of valuable components extraction.

More than 50 soil samples collected in the industrial facilities area (dams, hydraulic structures, sludge storages, etc.) from a depth of 5, 20 and 50 cm were studied. The chemical properties of soils were studied by standard techniques [1]. The bulk content of such elements as Cu, Ni, Zn, Pb was determined on a Perkin Elmer-5000 atomic absorption spectrometer. PP contents were determined by gravimetric and spectral analysis. The pH values of soils salt extracts were obtained with the usage of a potentiometer. Statistical data processing was carried out in Microsoft Excel.

Discussion. According to modern concepts, the geochemical barrier is an open, non-equilibrium, dynamic, self-organizing system with many factors determining the fixation of elements. The migration intensity and elements accumulation on geochemical barriers depend primarily on the pH of the medium, the ionic composition of the soil, the presence of organic compounds and sorption materials, and salinization. The table shows the distribution of the main ions, pH values, the content of HM and PP in the soil to a depth of 50 cm on the territory of one of the studied technogenic objects, up to 500 m away from the pollution source.

The determined soils pH values reach 8-9, which means that soils are alkaline. This differs significantly from natural criteria and indicates the saturation of soil substrates with bases. This causes a decrease in the soil resistance to the proton load and it's high sensitivity to interaction with metals. Figure 1 shows the dependences of the chemical element content on the soil pH using the example of Cu and Pb. Correlations should be interpreted as confirmation of metals accumulation during soil alkalization. The identified process indicates the accumulation of metal on the alkaline geochemical barrier.

As a rule, soils in the mining area, sludge, and tailing dumps serve as soil and groundwater constant salinization source. The soils chemical analysis have shown high concentrations of chlorine ions Cl^- up to 68.9 mg/dm^3, and SO_4^{2-} ions up to 197 mg/dm^3.

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Chemical analysis of soil in the technogenic area, the content of petroleum products, heavy metals (mg/kg), ions (mEq/100 g of soil)

Sample (distance from object, m)	Sampling depth, cm	Parameter									
		Ca^{++}	Mg^{++}	Na^{+}	K+	pH	Cu	Ni	Zn	Pb	PP
1 (50)	5	1.80	0.68	5.76	2.26	8.9	29.18	49.30	48.23	50.12	1.05
	20	1.20	0.57	3.78	2.47	8.8	37.25	83.15	55.60	59.89	1.19
	50	1.07	0.50	2.75	2.34	8.2	48.89	79.12	70.12	65.70	1.77
2 (150)	5	1.94	0.75	5.02	2.46	8.8	35.15	40.25	46.18	49.25	0.95
	20	1.35	0.60	4.03	1.98	8.7	44.12	73.49	60.50	58.26	0.99
	50	1.15	0.54	3.20	2.02	8.7	51.16	69.90	65.89	65.14	1.25
3 (350)	5	1.89	0.74	4.96	3.04	8.9	38.98	39.12	55.15	49.62	0.99
	20	1.30	0.66	3.89	2.60	8.5	40.24	45.24	62.14	55.42	1.02
	50	1.09	0.52	2.92	3.01	8.2	56.52	53.32	72.06	60.34	1.42
4 (500)	5	1.96	0.69	5.89	3.02	8.8	36.15	28.54	40.30	40.23	0.97
	20	1.28	0.59	3.93	2.47	8.6	45.26	30.59	51.41	53.25	1.05
	50	1.02	0.49	2.89	2.96	8.0	50.92	35.60	59.50	59.90	1.35
TLV, bulk content of heavy metals	–	–	–	–	–	–	33	20	55	32	–

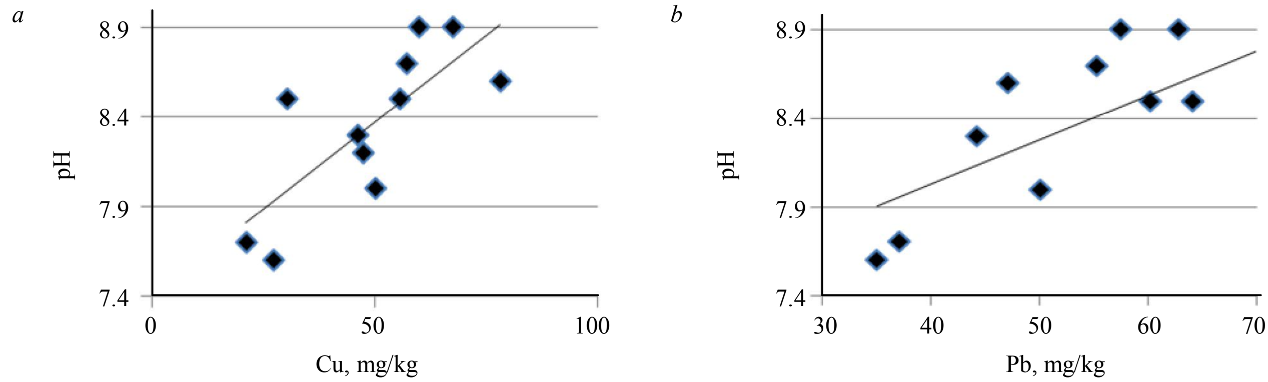

Fig.1. The dependence of Cu (*a*) and Pb (*b*) content in soils on pH value

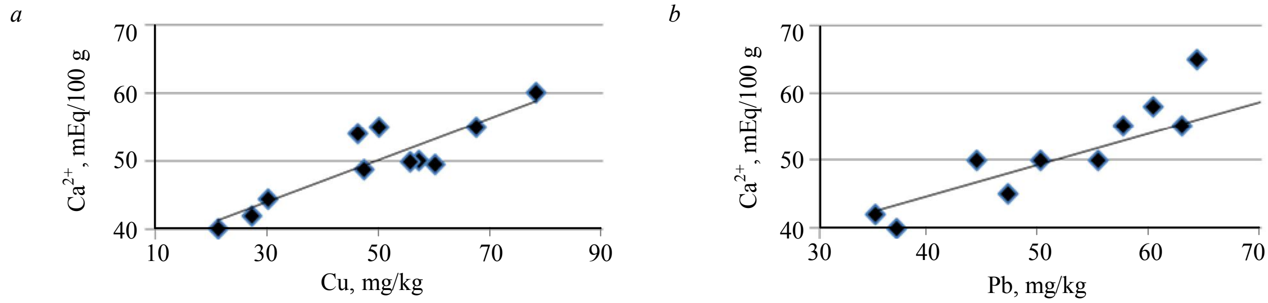

Fig.2. Dependence of Cu (*a*) and Pb (*b*) content in soils on Ca^{2+} ion concentration

Soil enrichment with SO_4^{2-} and Ca^{2+} ions can create conditions for the stable sulphate-alkaline geochemical barrier formation, which will inevitably cause fixation of some metals with their subsequent accumulation to concentrations exceeding TLV. Obtained correlations between the bulk HM content and one of the main cations confirm the author's assumptions, which is clearly illustrated by the example of Cu^{-} Ca^{2+} (Fig.2). This effect can be enhanced by the exchange interactions of HM with Na^{+}, K^{+}, Ca^{2+} cations.

It was also revealed that readily soluble sulfate and chloride salts penetrate along the soil profile to a depth of 30-50 cm (see table). The Cl^{-} and SO_4^{2-} ions concentrations are at the border of the toxicity index, and the Cl^{-}/SO_4^{2-} ratio is within the value of 4.33, which indicates soil salinization.

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It is known that absolutely all mining industries use petroleum products for a very wide range of work. Currently, the pollution of the earth's surface with petrolium and petrolium products has acquired a global scale, and the determination of the petroleum products content in soil and water is a priority in monitoring. The table shows the excess of the PP contents in the studied soils above the allowable concentrations. It should be emphasized that different climatic zones and different soil types require the use of different TLV values for petroleum products – 100; 300; 500 mg/kg. The presence of PP in the soil degrades its physical and chemical properties, impairs the nitrogen regime, leads to a change in oxidizing conditions to reducing ones. In the case of our study, it was also necessary to assess how salt contamination affects the PP distribution.

Regression analysis allowed us to obtain a quantitative dependence of the PP content on the amount of toxic salts Σ_{tox}: $y = 0.008x + 0.203$; $r = 0.82$; $n = 30$. The strong direct correlation explains the interdependent geochemical effect of the PP accumulation in the soil layer up to 30-50 cm in thickness accompanied by the salinization process. This is important for the development of scientific ideas in soil geochemistry, and also has practical significance for the potential exploration of the PP artificial geochemical barriers. The presence of a clay sorption layer that is active with respect to hydrocarbons can serve as a limitation on the further PP migration.

Conclusions. The diagnostic environmental geochemical signs of soils alterations in the technogenic area, were revealed, which relates to the change in their ionic composition and alkalinization. The medium pH values play the key role in the elements fixation in the soil layer. This creates favorable conditions for the formation of a stable alkaline geochemical barrier promoting chemical elements concentration. A direct quantitative correlation between the Cu and Pb accumulation, the acid-alkali properties of the soil, and the content of Ca^{2+} ions was also revealed. The accumulation of metals in the soil layer is enhanced by an additional sulfate-chloride pollution, as well as exchange interactions with Na^+, K^+, and Ca^{2+} cations. The observed effect is important for the development of ecological and geochemical monitoring in mining areas and also has practical significance for the potential metals exploration from soils in technogenic area.

The detected signs of a spontaneously formed technogenic barrier demonstrated the potential for development of artificial geochemical barriers on the migration path of technogenic elements and substances. In the context of the increasing shortage of valuable components for the number of industries, this approach can be assessed as attractive and innovative.

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