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Geochemical approach in assessing the technogenic impact on soils

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The soil assessment was carried out in the technogenically-affected area of Irkutsk Oblast with the geochemical approach as a key geoecological method using physical and chemical techniques of analysis and ecodiagnostics. Diagnostic signs of the disturbed natural properties of the soil were revealed up to a depth of 40 cm in the profile based on macro- and micromorphometric parameters. The content of heavy metals (HM) – Pb, Zn, Hg, and Cu with an excess of standards was determined, and empirical HM – pH correlations were obtained by statistical clustering of the data array. The contributions of additional factors affecting the chemical element distribution in the soil layer were investigated. Significant soil contamination with sulfates and the possibility of implementing the ion-exchange of HM and SO_4^{2-} for element immobilization were revealed. It was shown that reactions with sulfates and the influence of pH, HM exchange processes involving mobile K and P can determine the nature of the described chemical element distribution in the multi-factor-contaminated technogenic soil. However, the effectiveness of such types of interaction is different for each metal and also depends on the quantitative ratio of substances and soil characteristics, even under a minor change in pH. Two-parameter correlations of HM distribution in sulfate-contaminated soils confirmed the different degrees of involvement of chemical elements in these types of interactions. The results obtained and the identified factors are of applied significance and can be used as the basis for geoecological differentiation of the contaminated soil, as well as for determining local geochemical fields in the technogenesis zone. Areas of advanced research are related to three-dimensional modeling for a more complete study of the cause-and-effect relationships of geochemical parameters.

Key words: geochemical parameters; soils; technogenic objects; pollutants; heavy metals; sulfates; empirical dependencies

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Introduction. The development of new approaches to geoecological assessment of dynamically changing natural geosystems under the influence of increasing technogenesis is an urgent problem [2, 11]. Research and monitoring of soil conditions indicate a dangerous global trend of increasing concentrations of heavy metals (HM). Contamination of the Earth's surface and geological environment with heavy metals is global and most acute in the mining sites, in the territories of large industrial agglomerations, raw material processing plants, metallurgical, and fuel and energy complex [8, 13]. As a result, dangerous endogenous processes occur there, and local geochemical anomalies with a high content of toxicants are formed. A large number of studies have been devoted to the distribution of gross forms of HM in the environment and factors affecting it [10, 12]. A significantly fewer number of publications consider the behavior of mobile and ionic forms of HM, which mainly cause migration processes [9]. Given the multicomponent nature of soil pollution, it is necessary to assess the distribution of HM and migration properties taking into account different occurrence forms, key indicators of technogenically-altered soils (Technosols), the presence of other substances, and processes occurring in the soil layer.

The identification of the causal relationship between the HM distribution and the geochemical parameters of soils in the presence of other reactive toxicants determines the scientific and practical interest in the study of the problem. It is fundamental and multifaceted, and the lack of systematic understanding of the impact of a complex of unaccounted factors on the behavior of HM in technogenically disturbed soils and landscapes makes such research very relevant [5, 13, 14, 16].

In recent decades, in addition to global soil contamination with HM, the persistent sulfurization of soil cover, especially in the Northern hemisphere, has also been of particular concern as a result of the addition of sulfur compounds to emissions deposited on the soil cover as dry and wet industrial precipitation. The sulfate ion is the dominant acidic anion in the ion precipitation balance; it makes up to 31 % of the total precipitation on the surface for all EMEP observation stations (Co-operative Programme for Monitoring and Evaluation of the long-range Transmission of Air Pollut-

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ants in Europe). In particular, in Russia, the average annual concentration of sulfate ion can reach up to 0.41 mg/dm^3 at the Yaniskoski, Pinega, Danki, and Lesnoy Zapovednik control stations.

The review of scientific and regulatory literature has shown that there is no single method for assessing the state and degree of transformation of technogenically altered soil properties. The identification of criteria for the state of disturbed soils, taking into account the types of interactions in the soil substrate and possible transformations, starting from the analysis of composition and contents and up to the ion-molecular level of consideration and inter-phase interactions is an important scientific task in geochemistry and geoecology. Research is also relevant in terms of ensuring environmental safety since the formation of zones of accumulation of toxicants and the formation of geochemical anomalies of technophilic elements in soils can lead to the closure of cycles of migration of chemicals in the biosphere.

The purpose of this research is to identify and justify the dynamics of the distribution of such heavy metals as Pb, Zn, Hg, and Cu in conditions of multicomponent contamination, primarily with sulfates, taking into account the key parameters of the state of technogenic soils and possible ion-exchange processes based on the geochemical approach in geoecology using physical and chemical methods and techniques of soil ecodiagnostics.

Objects and methods. The research methodology was based on the theoretical foundations of the geochemistry of A.P. Vinogradov, G.V. Dobrovolskiy, N.S. Kasimov, and others [6].

Soils affected by heavy metals and sulfur compounds (sulfates) emitted from industrial facilities in Irkutsk Oblast were studied.

The subject of the study and main objectives:

• determination of disturbance criteria for natural properties of technogenic soils;

• analysis of the distribution of gross and acid-soluble forms of HM in soils;

• identification and interpretation of empirical dependencies of geochemical parameters of soils simultaneously contaminated with HM and sulfates.

Field surveys of the territory were used, three soil sections (and profiles) were obtained in the zone of industrial facilities, and chemical and ionic composition of more than 80 soil samples was determined. Soil samples were taken using a standard method from depths of 5-40 cm along the perimeter of industrial sites. The Perkin Elmer-5000 atomic absorption spectrometer (GOST 17.4.4.02-84; GN 2.1.7.2041-06; GN 2.1.7.2042-06) was used to determine the contents of heavy metals (gross and acid-soluble forms) Pb, Zn, Hg (hazard class 1), and Cu (hazard class 2). The pH values of salt and water extracts of soils were determined potentiometrically and Excel was used for statistical processing. The quality of analysis was assessed based on the results of external and internal control. The statistical observations and reports of the State Control of Irkutsk Oblast were used for comparative analysis with the obtained results.

Results and discussions. By its potential, Irkutsk Oblast is one of the few regions where all types of fuel and energy resources are available: more than 70 % of all-Russian reserves of coal, oil, fuel gas, 10 % of hydro and mineral resources, forest lands, etc. In 2017 alone, 91 licenses were issued for the use of mineral resources, including 16 for hydrocarbon raw materials and 49 for placer and ore gold; mining operations were carried out at 194 sites. The combination and diversity of industries was a prerequisite for the development of energy, non-ferrous and ferrous metallurgy, mining, petrochemical, pulp and paper, and other economy sectors. This led to the high density of industrial facilities, the creation of a complex of heat and power plants, intensified use of motor transport, and production of paper, chemicals, and detergents.

A comparative analysis of mining dynamics in 2007-2018 revealed an increase in the volume of incoming pollutants from the industry, primarily heavy metals and sulfur-containing compounds [3, 4]. Thus, in industrial cities of the region, soils are contaminated with such HM as Pb, Cd, Zn, and Hg,–sometimes with 80-100 % excess of the Russian maximum permissible concentrations (MPC) in all samples. In soils in the area of Ust-Ilimsk, there is an excess of MPC of Pb, Cd, and Zn in 70 % of the samples taken. In this case, Pb and Zn are distributed in a zone over 5-20 km from the source, for example, from PJSC RUSAL Bratsk.

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For the Baikal region (for example, at the Listvyanka observation station), the content of the sulfate ion is five or more times higher than the background levels. The average content of exchange sulfates in soils was up to two MPC, and the proportion of soils with the levels exceeding this threshold was up to 58 %. The average content of exchange sulfates in the surveyed soils of some territories of Irkutsk Oblast was from 193 to 365 mg/kg, the content of sulfur dioxide and hydrogen sulfide in residential areas is 10-20 times higher than the established standards [1]. The combination of significant amounts of HM and reactive sulfate compounds in the soil layer creates prerequisites for active chemical transformations, which must be taken into account in the geochemical assessment of the territory during geoecological analysis.

As an initial stage of the work, key geochemical indicators in a profile of 40 cm were determined using the example of three soil sections (Table).

Geochemical properties of soils and sediments in three sections

Soil pit	Depth, cm	Organic carbon, %	pH H_2O	Absorbed			Mobile		Carbonate CO_2, %
				Ca^{2+}	Mg^{2+}	сумма	P_2O_5	K_2O	
				milligram-equivalent per 100 g of soil			milligram per 100 g of soil		
1	5-10	7.1	9.5	19.5	13.7	33.2	10.8	97.1	0.544
	10-20	4.6	8.0	17.3	4.2	31.5	6.5	52.5	0.096
	20-40	1.3	7.5	8.9	5.8	14.7	3.2	5.6	0.100
2	5-10	5.0	8.8	18.4	10.6	20.0	3.5	38.0	0.428
	10-20	1.7	7.0	8.7	4.0	10.0	15.0	2.0	0.124
	20-40	0.5	5.9	8.0	2.7	9.4	10.8	1.2	0.064
3	5-10	4.8	9.2	18.4	12.1	26.2	12.4	184.0	0.450
	10-20	2.1	8.5	12.6	7.3	19.9	26.8	30.0	0.098
	20-40	0.8	6.9	–	–	–	–	–	0.052

The table shows that the organic carbon content is low and quickly decreases as depth increases, from 7 to 1.3 %, the carbonates content is raised to 0.544 % and the pH values are up to 8.8-9.5. The alkaline nature of soils does not provide buffer properties when receiving HM. For comparison, the pH values should be given for natural (clean) soils, for which the pH is 4.5-6.0. The difference between the pH of an aqueous extract and pH of a salt extract is equal to 0.5-1 and alkalization results in the formation of an active ion-exchange complex in the surface layer of the soil and the possibility of chemical transformations with the participation of HM. This also confirms the absorption capacity (the sum of exchange cations) – 33.2 milligram-equivalent per 100 g of soil, while for pure sod-podzolic soils it does not exceed 10-15 milligram-equivalent per 100 g of soil. In the composition of exchange cations, the main share belongs to calcium; there is an accumulation of mobile K up to 97-184 and P up to 26 mg/100 g of soil, respectively, may be due to aerogenic input, for example, ash from fuel combustion, mineral particles from transportation and dusting of rocks, construction materials, etc.

One of the key factors affecting the distribution of chemical elements in the soil layer and their migration ability is the pH of the environment. For such metals as Hg, Pb, Zn, and Cu, distributions of their mobile (acid-soluble) forms and the pH of the soil layer were determined in 80 soil samples (Fig.1). Statistical data processing revealed the automatic splitting of the elements of the set into certain groups (clusters). Cluster analysis can identify either common features or differences in the behavior of chemical elements. Cluster analysis is a new rapidly developing branch of modern theoretical computer science that allows us to significantly expand the capabilities of data processing and interpretation.

The results obtained by a high level of aggregation allow us to conclude that an additional factor regulates the dynamics of the behavior of chemical elements in the Technosols. The ion-exchange process of HM with mobile potassium and phosphorus, which concentrations differ in soil samples (Table) may be one of these factors.

The data from an aqueous extract of the Technosols, where there was a systematic excess of the content of sulfate ions up to 0.6 milligram-equivalent per 100 g of soil, allowed to thoroughly

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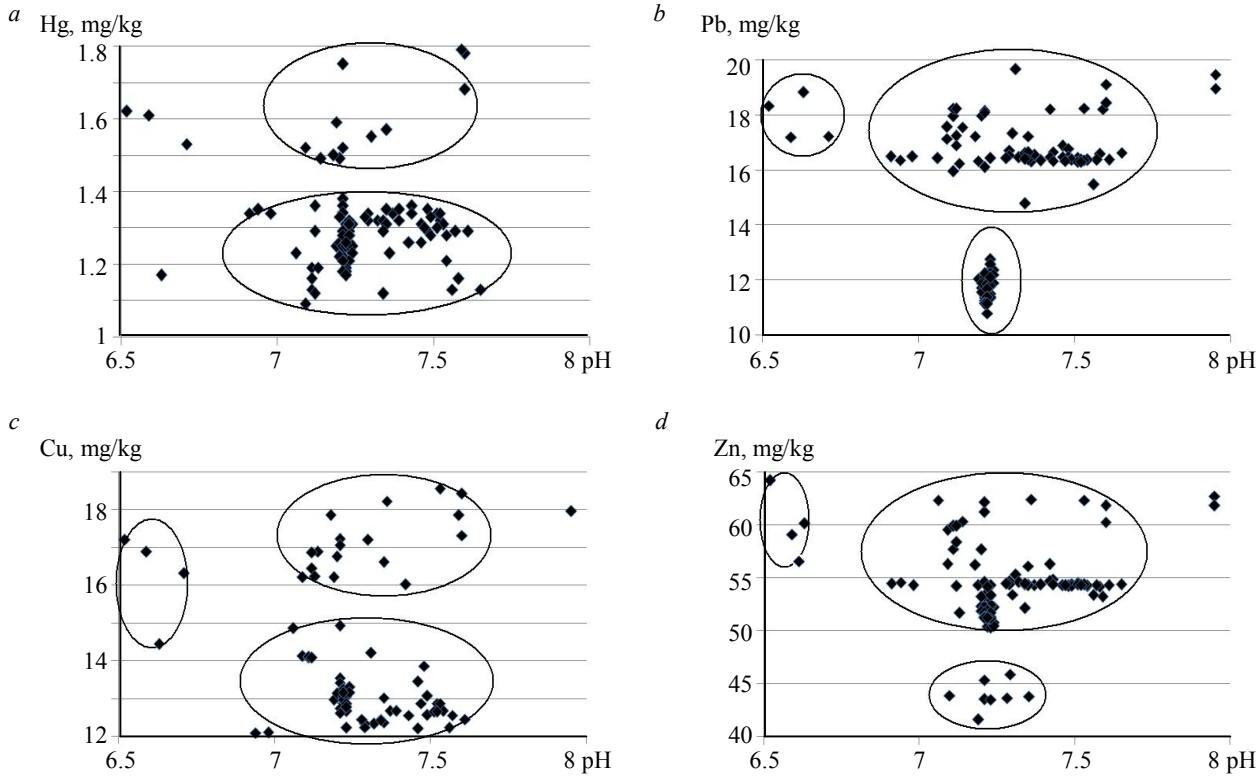


Fig.1. Distribution Hg (*a*), Pb (*b*), Cu (*c*), and Zn (*d*) related to pH

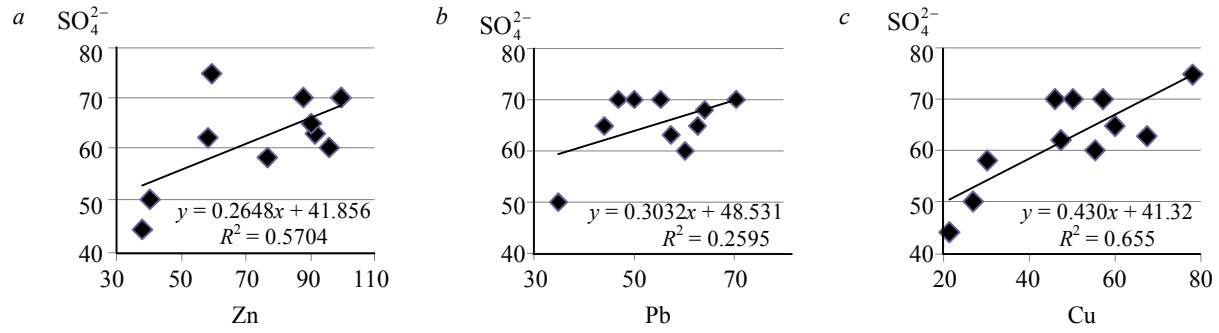


Fig.2. Distribution dynamics of Zn – SO_4^{2-} (*a*), Pb – SO_4^{2-} (*b*), and Cu – SO_4^{2-} (*c*) in the technogenic soil

describe the picture of HM distribution into clusters. This can significantly affect the chemistry of transformations involving HM since sulfates (SO_4^{2-}) are not only highly sensitive to the pH level of the medium but also enter into exchange reactions with metals to form new compounds and complexes [7]. This factor can be an additional contribution to the formation of individual clusters in the distributions shown in Figure 1. Sulfates have high solubility, mobility, can be oxidized and undergo various transformations, in particular, with the formation of mobile hydrated, ionic forms of metals or fixed complexes [15, 16]. The empirical dependences shown in Fig.2 are a convincing example demonstrating the high sensitivity of the distribution of Zn, Pb, and Cu to the content of the sulfate ion in the soil. The coefficients of determination R^2 vary for the three elements from 0.2595 to 0.6555, which confirms their different sensitivity when interacting with sulfate ions and the different probability of formation of fixed forms in the HM series.

Sulfates significantly reduce the mobility of copper, with which it easily forms insoluble CuS sulfide and, the higher the concentration of sulfate ions, the greater the degree of immobilization of copper, which is demonstrated by a satisfactory correspondence in Fig.2 *c*. But in reducing conditions, the mobility of copper can be, on the contrary, decreased. This contributes to the formation of local geochemical fields; as a result, distribution clusters are found. The effectiveness of binding

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with sulfates for zinc and lead is slightly lower. For lead, the presence of phosphates in the soil is equally important when its mobility is reduced. In other words, the identified features of HM distribution in the technogenic soil are mainly due to the course of exchange processes with sulfates and mobile K and P, as well as the ratio of concentrations of the analyzed components (or state parameters).

For in-depth analysis of the behavior of heavy metals in anthropogenically modified soil layer and identification of causal relationships in geochemical parameters of soils in geoecological analysis of territories in the zone of technogenesis, the use of three-dimensional computer model in parameters, for example, HM-pH-SO_4^{2-} is a challenge for further advanced studies.

Conclusion. Based on analytical, macro- and micromorphometric signs of changes in the soil layer, the diagnostic signs confirming the technogenic nature of the formation of geochemical parameters in the conditions of HM and sulfate contamination were obtained. The cause-and-effect relationships between the parameters pH – HM content, sulfate-ions – HM content were identified, and the mutually determining factors of their behavior were analyzed, taking into account the properties of the soil layer. This makes it possible to predict migration flows of HM (their mobility or immobilization) in technogenically disturbed geosystems. Research shows the need to take into account the distribution functions of pollutant components in soils based on exchange ion interactions with sulfates and mobile K and P. For each metal, the effectiveness of such interaction is different and depends on the quantitative ratio of pollutants in the soil substrate, even within the same pH value. The identified factors can be used as the basis for soil differentiation and for the detection of local geochemical fields in the zone of technogenesis, which is of practical significance. The directions of prospective research involving three-dimensional modeling for a more complete study of the cause-and-effect relationships of the behavior of geochemical parameters for technogenic soils are indicated.

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