Ecogeochemical evaluation of soils under conditions of technogenesis

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Abstract. The distribution of total forms of heavy metals Cu, Cd, Ni, Pb, Zn, Co, Hg, and As in technogenic soils has been evaluated using geochemical research methods. Diagnostic indicators of damage of soil natural properties in the area of technogenesis are revealed. Statistically significant empirical dependences toxic elements migration on the buffer properties of soils (pH, N, C_{org}) and salinity factor of the territory are obtained. It is shown that in the zone of industrial objects in the soil surface layer, lateral technogenic geochemical pollution modules can be formed at depth down to 30-50 cm. This should be taken into account when evaluating the environmental risk of a territory and in the environmental control of soil pollution.

1. Introduction

Technogenesis is a process involving significant changes in natural complexes as well as in properties of landscapes, soils, surface- and groundwater. Under the influence of industrial activity, the scale of technogenesis increases and becomes global [1,2]. The effect of combined geochemical processes associated with technogenic human activity is accompanied by unpredictable migration, concentration and transformation of chemical compounds and elements in the soils of technogenic zones [3]. Therefore, ecogeochemical evaluation of soils represents an urgent challenge, which is caused by the requirementsto environmental safety of territories, analysis of the industrial production and assessment of the soil-ecological state of technogenic landscapes [4].

No less significant is an issue related to obtaining the correct diagnostic indicators and quantitative criteria of damage of soil natural properties in anthropogenically disturbed landscapes [5]. The methodology of natural objects ecodiagnostics is now at the stage of development and accumulation of systematic results.

Therefore, obtaining new data in this area certainly contributes to the development of approaches to evaluation of the negative impact of technogenesis on biospheric objects and, in particular, on soils [6].

It is known that pollution and damage of soils natural properties is caused by the migration of technogenic substances and chemical elements. Consequently, the search for evidences of their mobility (or fixation) under the conditions of technologically changeable environment is a topical task for landscape geochemistry and geocology [7,8].
Since soils are deposit media and they reflect the destructions in natural geochemical cycles under the negative effect of industrial facilities, their physical-chemical properties and ecological state can be accompanied by the formation of geochemical anomalies in the presence of pollutants. The found criteria of such a state will serve as indicators of the level of anthropogenic impact on a territory. Geochemical analysis using physical-chemical research methods constitute a basis for addressing the above challenge.

The purpose of the present work is to evaluate the distribution of total and mobile forms of heavy metals Cu, Cd, Ni, Pb, Zn, Co, Hg, and As in the technogenically damaged soils in the area of industrial facilities using geochemical research methods. These elements are included in the priority list of controlled pollutants. It is also important to elucidate the changes in basic buffer properties of the soils, which can serve for assessment of the level of their natural properties damage [9].

2. Materials and methods

The research methodology was based on the geochemical approaches developed by A.P. Vinogradov, G.V. Dobrovolsky, N.S. Kasimov.

Objects of the study (soil samples) were taken in the zone of hazardous production facilities (thermal power plants, tailings dams, hydraulic utilities, tank farms, etc.) on a control network from a depth of 5, 20 and 50 cm in accordance with rules for samples selection in Russia and chemical analysis of soils (Russian State Standards 17.4.4.02-84 and GOST 17.4.3.01) [10].

The contents of total forms of chemical elements were determined on a Perkin Elmer–5000 atomic absorption spectrometer. The following soil-geochemical indicators of the state were determined: organic carbon (C_{org}), total nitrogen (N_{tot}) were analyzed “according to Tyurin”, pH values of salt and water extracts of soils were obtained potentiometrically. The main ions Ca^{2+}, Mg^{2+}, Na^{+}, Cl^{−}, SO_{4}^{2−}, HCO_{3}^{−} were determined in aqueous extraction of soils [11]. All methods used are standard and generally accepted in geochemical soil analysis.

Statistical processing was carried out on the basis of the software package statistics in Excel.

3. Experimental

The accumulation of chemical elements depends not only on the properties of these elements, which are concentrated in one geochemical environment and are non-mobile (inactive) in another [12, 13, 14]. The intensity of migration, accumulation (concentration) of elements in the soil changes due to alteration in the parameters of the ecological state of the soil. These are, first of all, the pH of medium, the presence of organic compounds and sorption materials in the soil layer, the ion and salt composition, etc. Therefore, key parameters of soils in the zone of hazardous production facilities have been experimentally determined and analyzed in this work.

For example, Figure 1 shows the distribution of soil pH_{aq} values in 11 sampling sites in the area of an industrial enterprise at a distance of 500 m from the object along the perimeter. It is found that soil layer has mainly alkaline character, which is formed due to atmospheric precipitation, construction and road dust.
The soil absorbing layer shows a steady increase in calcium and magnesium salts in the form of ions. Thus, for 11 sampling sites in the enterprise zone, the average content of such salts in the aqueous extract is more than 20.89 mg-equiv/100 g of soil for calcium ions, and 12 mg-equiv/100 g of soil for magnesium ions. This leads to alkalization of the soil layer and, as a consequence, to the increase of pH.

It was also revealed that the relative content of Cl⁻ / SO₄²⁻ ions is on the border of the toxicity index - 4.33 and contributes to chloride-sulfate salinization of the soil layer.

The content of carbonate ion HCO₃⁻ in the studied soils does not exceed 0.3 mg-equiv./100 g of soil, and that of Na⁺+K⁺ is not higher than 0.2 mg-equiv./100 g of soil.

Two other very important indicators of the soil ecological state reflect their protective buffer function. The total nitrogen content (N$_{tot}$) is one of the criteria for natural geochemical level and, along with total carbon content (C$_{tot}$) determines the natural soil-forming process. The C:N ratio is a criterion of nitrogen concentration in the soil pool, which characterizes the presence of humus (fertile layer).

A chemical analysis of the soil in the layer from 0 to 30 cm reveals for almost all samples a deterioration of the nitrogen regime of the soil layer: the content of N$_{tot}$ does not exceed 0.065–0.115%, and the ratio C/N ranges 25-50. For natural soils, this ratio usually is not higher than 10.

4. Results and discussion

The accumulation of elements also depends on the properties of these elements, which are accumulated in one geochemical environment and are less mobile in another. The contents of the studied series of elements have been determined. Accumulative associative series are calculated to confirm different concentration of these elements in soils at a distance of 500 m from the object at a depth of soil section from 5 to 30 cm as follows:

- 0-5 cm: Cr$_{13.05}$ → Co$_{12.97}$ → Zn$_{11.14}$ → Pb$_{11.03}$ → Ni$_{10.95}$ → Cu$_{10.46}$ → Mn$_{10.08}$
- 5-10 cm: Cr$_{13.05}$ → Co$_{11.99}$ → Zn$_{10.99}$ → Pb$_{10.77}$ → Ni$_{10.68}$ → Cu$_{10.47}$ → Mn$_{10.07}$
- 10-15 cm: Cr$_{15.23}$ → Co$_{14.74}$ → Ni$_{10.96}$ → Zn$_{10.96}$ → Pb$_{10.77}$ → Cu$_{10.47}$ → Mn$_{10.08}$
- 15-30 cm: Cr$_{17.40}$ → Co$_{12.26}$ → Zn$_{10.95}$ → Ni$_{10.95}$ → Pb$_{10.77}$ → Cu$_{10.41}$ → Mn$_{10.08}$

Comparative analysis of the distribution of TM and the obtained parameters of soil state (for example, pH) allows statistically significant dependencies to be determined. Thus, the antibate
character of trends in the distribution of various chemical elements depending on pH is found. For instance, for pairs of As, Cu and Cd, Hg, asynchronous dependencies of total on soil pH are revealed (Figure 2 and 3).

Figure 2. Dynamics of Cd and Hg content in soil depending on pH.

Figure 3. Dynamics of As and Cu content in soil depending on pH.
It is seen that even slight variations in pH values affect the behavior and ability to accumulation of various chemical elements in the soil layer. In addition, a low content of nitrogen can decrease the buffer activity of the soil layer and increase the mobility and migration of toxic elements.

The presence of exchange interactions of chemical elements with Na\(^+\), K\(^+\), Ca\(^{2+}\), SO\(_4^{2-}\) cations also promote to the different mobility and complex formation of TM in the soil layer. Figure 4 shows dynamics of metalZn distribution depending on concentration of sulfate ions in the soil.

\[ y = 0,2648x + 41,856 \]  
\[ R^2 = 0,5704 \]

**Figure 4.** Dynamics of Zn–SO\(_4^{2-}\) distribution in technogenic soil.

5. Conclusions
The geochemical analysis in the area of technogenic objects has revealed accumulative series of chemical elements in the soils. It is established that abnormal fields of soil contamination with heavy metals are formed at a depth of 30 cm. Geochemical analysis has also shown a damage of natural buffer properties, alkalinization of the soils, impoverishment of N, and chloride-sulphate salinization of territories. From a fundamental point of view, the revealed regularities of the distribution of technogenic chemical elements, determination of cause-and effect relationship of ecogeochemical parameters contribute to the understanding of the pollutants migration under the conditions of technogenesis. These studies are promising for forecasting the environmental emergencies of a technogenic nature, which is consistent with the requirements of the state control of the soil environmental safety during the development of natural territories. The results obtained contribute to the development of biospheric sciences, in particular, soil ecology, geocology and geochemistry [15, 16, 17].

References
[1] Osipov VI 2016 Global environmental problems Technogenesis and modern problems of earth sciences *Ecology and Industry of Russia (EKIP)* 3 pp 4–12
[2] Siromlya T I 2009 On the question of mobile forms of compounds of chemical elements in soils *Siberian Ecological Journal* 2 pp 307–318
[3] Kosheleva N E, Kasimov N S, Vlasov D V 2015 Factors of the accumulation of heavy metals and metalloids at geochemical barriers in urban soils *Eurasian Soil Science* 48 5 pp 476–492
[4] Gradner M, Gunn A 1989 The effect of natural ligands on trace metal partitioning *Chemosphere* **19** 8-9 pp 1251–59

[5] Androkhanov V A, Kurachev V M 2009 Principles for evaluating the soil-ecological state of technogenic landscapes *Siberian Journal of Ecology* **2** pp 165–169

[6] Opekunova M G, Opekunov A Yu, Kukushkin S Yu, Arestova I Yu 2018 Evaluation of the transformation of the natural environment in the areas of hydrocarbon development in the north of Western Siberia *Siberian Journal of Ecology* **1** pp 122–138

[7] Bunzl K, Trautmannsheimer M, Schramel P 1999 Portioning of heavy metals in a soil contaminated by slag: A redistribution study *Journal Environmental Qual* **28** 4 pp 1168–73

[8] Sarapulova G I 2018 Ecological-geochemical evaluation of soils in the area of technogenic objects *Notes of the Mining Institute* **234** pp 508–512

[9] Tuner M G, Gardner R H, O'Neill R V 2001 *Landscape Ecology in Theory and Practic* (Springer-Verlag, New York, NY, USA) p 401

[10] Arinushkina E V 1970 *Manual on chemical analysis of soil* (Moscow: Moscow State University) p 487

[11] 1980 *Physical-chemical methods of soil research* (Moscow: Moscow State University) p 250

[12] Sanderson J, Harris L D 2000 *Landscape Ecology: A Top-Down Approach* (Lewis Publishers, Boca Raton, Florida, USA) p 246

[13] Glazovskaya M A 1999 Problems and methods for evaluation of ecological and geochemical stability of soils *Soil science* **1** pp 114–124

[14] Wu J 2006 Cross-disciplinarity, landscape ecology, and sustainability science *Landscape Ecology* **21** pp 1–4

[15] Gambrell R P, Wiesepape J B, Patrick W H, Duff M C 1991 The effects of pH, redox and salinity on metal release from a contaminated sediment *Water, Air and Soil Pollut* **57-58** pp 359–367

[16] Dergacheva M I 2019 Soil ecology: the formation of a new biosphere class science *Siberian Journal of Ecology* **2** pp 143–150

[17] Kocharyan A G, Lebedeva I P 2015 Diffuse sources of pollution in catchment areas and assessment of their toxic effects on water and soil ecosystems *Environmental Management* **5** pp 40–45