Computer Modeling of Zn and Ni Distribution in Technogenic Soils

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Abstract. Based on computer modeling using geochemical parameters, new results of the interdependent distribution of mobile forms of heavy metals Zn and Ni in contaminated soil have been obtained. Modeling in Golden Software SURFER 8 made it possible to identify soil contamination halos - laterally module - in the zone of a hazardous gas station facility in the city. A three-dimensional skeleton model of the distribution of mobile forms of HM was obtained depending on the key parameter of soil organic carbon - Corg. The revealed picture of the distribution of metals adequately reflects the specificity of the individual chemical properties of Zn, Ni and clearly demonstrates the different efficiency of binding of their mobile forms with soil organic matter. The proposed approach of computer geochemical modeling can be recommended as a methodological guide for identifying the characteristics of behavior in the soil environment for other heavy metals. The revealed empirical dependencies prove the need to change approaches in the ecological assessment of territories in the conditions of technogenesis. Research also has a promising development, allows one to obtain new geochemical patterns and associations of elements in technogenic landscapes, which contributes to the development of the fundamental foundations of geochemical science.

1. Introduction

The increasing “metallization” of the biosphere as a result of the technogenic influx of heavy metals (HM) into environmental objects makes it necessary to study the behavior and transformation of these toxic elements [1]. Sources of HM entering soils, surface groundwater, plants are the burning of fossil fuels, metallurgical production, abrasion of transport brake pads, mining and processing of minerals and polymetallic ores, railways, metal-containing production and consumption wastes in landfills, etc.

For a number of years, the dynamics of growth in the HM content in soils has been recorded in the Russian Federation, especially in the technogenesis zone. The increase in HM contents in natural landscapes and in anthropogenic areas of territories is accompanied by a violation of the protective function of soils and changes in global geochemical cycles. This is most noticeably manifested at the regional level in the area of operating enterprises and industrial facilities, extractive industries, old tailing dumps, dumps and other technogenic formations [2, 3].

The processes of technogenic migration, geochemical transformation, immobilization, complexation, ion exchange with the participation of HMs can lead to the formation of spontaneous geochemical barriers in the soil layer, on which significant contents of toxic elements that are not taken into account by environmental control accumulate [4].
To ensure environmental safety and risk assessment, it is necessary to study the features of the spread of HM and forecast the development of negative consequences as a result of contamination of territories with these toxicants. Research in this area has become very active in recent years [5, 6]. For geoecological and geochemical assessment of territories, various approaches are involved, physicochemical, analytical, statistical methods, as well as techniques of imitation, experimental and mathematical modeling [7, 8].

Modeling geochemical processes in the technogenesis zone is especially important in the formation of technogenic deposits (and their constituent elements). This direction of geochemical research is a very urgent fundamental and strategic task in subsoil use, in mining and environmental sciences [9, 10, 11].

This is also a very promising direction in order to search for solutions for the subsequent recovery of lost useful products, including HM, that enter the soil and then accumulate in different parts of the development territory. Taking into account the complex composition of technogenically altered soils, their disturbed physicochemical properties and multifactorial impact on their state, a set of approaches and research methods are used to study such natural dynamic systems [12, 13, 14, 15, 16]. As a rule, these are spatio-temporal analysis, analytical methods of ecodiagnostics, geosystem geographic analysis, physicochemical studies, and the developing area of geochemical modeling [17].

As part of the system analysis, modeling techniques make it possible to obtain a spatio-temporal characteristic of the ecological situation in the technogenesis zone. Modeling also makes it possible to obtain an explanation and prediction of the behavior of TM under conditions when the theoretical level of research is insufficiently accurate. In this regard, modeling is also highly advisable for the selection of practical goals for the ecological transformation of huge disturbed territories as a result of their development.

The fundamental principles of modeling natural geosystems, including soils, make it possible to apply the structural-dynamic approach through, first of all, simulation. Based on the ratios of different empirical parameters and characteristics of this dynamic ecological environment, it is possible to identify the internal connections between its constituent elements and components. It is possible to describe the ongoing processes in the soil environment and link the identified elements of analysis into a single system of the state of the geosystem. This is especially necessary for the study of fundamental dynamic processes and identification of patterns of development of disturbed geosystems under conditions of increasing technogenic impact. In addition, the results of simulation based on empirical data are a sound scientific basis for planning practical activities in environmental management.

For example, it is possible to identify the direction of migration flows of various toxicants, describe the inevitable consequences of HM entering the soils of territories, and then develop protective technologies for their protection. It is the methods of geochemical modeling that make it possible to outline the prospective development of economical and rational use of natural resources and the territory as a whole.

Therefore, the use of methods of imitation and empirical modeling to describe the state of landscapes, geological environment, soils, water environment, atmospheric air is justified. In the context of increasing technogenesis, the identification of the degree of disturbance of natural geosystems using empirical models is very important.

It should be noted that discrete-continuous natural systems, including soils, are distributed dynamic systems consisting of a large number of elements. Modeling of physicochemical, including complex soil processes based on the identified parameters of their state at a certain point in time can reveal hidden relationships and interdependence of the behavior of the components of the soil pool, which cannot be done by other methods.

This is necessary to assess the environmental safety of the soil cover in areas of negative impact of industrial facilities.

For example, on the basis of the obtained patterns of HM distribution, it is possible to develop environmental protection measures for the rehabilitation of contaminated and disturbed lands, to select specific methods of neutralization, technologies for recultivation and cleaning of soils from toxicants.
Thus, computer geochemical modeling is a modern effective tool for assessing the environmental risks of environmental pollution, control and management of factors affecting their condition. This can significantly facilitate the adoption of nature management decisions for the purpose of environmental safety of territories.

It should also be noted that the search for patterns of migration and accumulation of pollutants in the soil, as well as understanding the mechanism of their transformation in a multicomponent structure, is dictated not only by modern requirements of environmental safety. This is also associated with the urgent need to revise the concept of standardization of chemical pollutants in geosystems, especially in soils - MPC (APC) [18, 19].

The lack of new approaches to the study of the behavior of HMs in technogenically altered soils, especially mobile and most toxic forms, determine the relevance of the research. Environmental monitoring of soil contamination with HM is usually aimed at determining the total content of gross fixed forms of metals, while it is the mobile forms that determine the migration characteristics of elements. They are the most reactive, determine the effectiveness of various types of physical and chemical interactions in the soil layer, are very sensitive to the parameters of the soil environment and the mutual influence of other substances. Unfortunately, studies of this kind involving mobile forms of HM are very limited and are at the stage of accumulating actual data.

The study of the mechanism of migration, accumulation of mobile forms of HM, the search for interdependent relationships and parameters of their distribution in soils in the technogenetic zone is the goal of the systematic geochemical studies carried out by the author. In this work, using a particular example of two chemical elements - Zn and Ni - the results of studying the peculiarities of the distribution of their mobile forms in technogenic soil in the zone of a hazardous industrial facility on the basis of empirical imitation modeling are presented.

Using the Golden Software SURFER 8 package, new models were obtained, which revealed the interdependent dependence of the Zn and Ni distribution in the soil on the parameters of the disturbed soil state.

2. Materials and methods
The objects of study were contaminated soils in the gas station area, through which a large number of cars pass. The gas station is located near a highway within a large city. Field work was carried out, more than 50 soil samples were taken to a depth of 20 cm in the zone of influence of the object in accordance with the standards. Soil sampling was carried out in accordance with GOST R 53123 2008 (ISO 10381-5: 2005) "Soil quality. Sample selection. Part 5. Guidelines for the study of urban and industrial sites for soil pollution "and GOST 17.4.4.02 2017" Nature protection. Soils. Methods of sampling and preparation of samples for chemical, bacteriological, helminthological analysis ".

In order to eliminate random errors associated with the determination of unreliable values, sampling with a mass of 500 g was carried out by the envelope method from 1 × 1 m sites. The choice of specific HM Zn and Ni was due to the fact that according to the data of state control over the past decades, up to 70% of urban and technogenic landscapes in terms of the content of technophilic HMs do not correspond to the environmental standards of MPC (MPC).

To determine the contents of gross and mobile forms of HM, atomic absorption spectrophotometry was used using a Perkin-Elmer 500. Gross forms of HM were isolated from soils by means of HNO3 extraction. Mobile forms of HM were isolated by decomposition and extraction from an acetate-ammonium buffer solution with pH = 4.8. The content of mobile forms of Ni, Zn in the soil is normalized by the maximum permissible concentration established by GN 2.1.7.2041-06. The determination of the organic carbon content was carried out according to Tyurin.

The geographic information system Golden Software Surfer 8 was used for modeling, which is currently the industry standard for plotting graphical representations of functions of two or three variables. The mathematical basis of the Surfer 8 package is formed by eight algorithms for interpolation of two-dimensional functions at the nodes of a regular grid using the initial data.
The advantage of this program is the interpolation algorithms embedded in it, which allow creating digital surface models and a three-dimensional image with the highest quality from data unevenly distributed in space.

With the help of Surfer 8, map diagrams and halos of HM distribution in contours with filling were obtained, as well as a three-dimensional wireframe model in the «Ni-Zn-Corg» parameters for contaminated soil in the zone of an urban gas station.

3. Research results

Usually, for the ecological assessment of the territory, the values of the gross forms of HM are traditionally used in accordance with the approved methods and standards of the MPC (APC). The gross content of HMs is one of the main and general indicators of the chemical composition used in assessing soil pollution. The work revealed that the contents of the gross forms of HM - Zn and Ni- in soil samples in the zone of influence of the production facility significantly exceed the established environmental safety standards - MPC for sandy loam soils (MPC gross for Zn = 32, and MPC for Ni = 33 mg / kg).

But in soils, in the general balance of chemical substances and elements, there are always mobile water-soluble forms of HM, which mainly determine the current content of soils, as well as the processes of migration and accumulation.

The concentrations of mobile forms of Zn and Ni in contaminated soil have been determined. Their values also exceeded the permissible environmental standards (MPCsub Zn = 3 mg / kg, for Nisub = 6 mg / kg). It is for these mobile forms of Zn and Ni that map diagrams and halos of their distribution in soils in the gas station zone were obtained: 1- reservoirs with oil products, 2- gas stations, 3- office, 4- city highway Figs 1 and 2.

It is known that the mobility, migration, and fixation of HMs in the soil substrate depends on many factors, among which the content of organic matter is dominant [20]. Chemical analysis revealed that, in the studied technogenic soils, the organic content is (organic carbon) Corg = 0.02-0.06%. Figure 3 shows a map diagram and halos of organic carbon distribution in the gas station area.

Figure 1. Schematic map and halos of mobile Ni distribution in contaminated soil in the area of the object.
4. Discussion

The excess of ecological standards for the content of gross and mobile forms of HM in the studied area led to an accumulative type of distribution with a profile depth of up to 20-40 cm. Concentration coefficients for a number of chemical elements in the studied soil were calculated, while the accumulation coefficient $K_c$ for most of the metals was mainly: 2.5 - 3.7 ($K_c$ should not exceed 1).
In addition, the cumulative associative array was also higher for Ni 5.7 - Zn 10.4, which indicates the emergence of a technogenic lateral modulus of contamination with these metals. In other words, a spontaneous technogenic geochemical anomaly is formed on the territory of cities as a result of HM pollution, which creates an increased environmental safety risk. Comparative graphical analysis of the distribution of mobile forms of Zn and Ni on the models in Fig. 1 and 2 revealed a different pattern and direction of pollution of the analyzed area.

Mobile soluble forms of HMs can either migrate along the soil horizons of territories, covering large areas, or interact with the components of the soil environment, settling in certain areas. In this case, the inactivation of mobile forms can occur, their subsequent accumulation - accumulation, fixation, which leads to the formation of pollution fields and the emergence of technogenic geochemical barriers. It is necessary to find out the reasons for their inactivation. Their fixation largely depends on the main parameters of the soil, including the pH and the content of organic matter - Corg.

The studied soils are characterized by increased pH values up to 8-9 units. An earlier analysis of the behavior of HMs from the acid-base reaction of the soil showed an almost identical reaction of these metals to the pH of the soil. That is why, as a rule, in practice, either liming (alkalinization of soils to increase the pH of the medium) or the introduction of organic matter is used to neutralize soils.

The superposition of the halos in Figs 1 and 2 on the map of the distribution of organic carbon in Fig. 3 revealed a significant difference in the dependence of the behavior of Zn and Ni on the concentration of organic matter. The process of metal fixation includes adsorption, sedimentation, coagulation, inter-batch absorption by clay minerals. The presence of organic matter is the most important factor affecting HM. The complexity of the chemical composition of the soil pool necessitates the correct choice of characteristics that are included in the modeling process.

To optimize the models, a different set of factors, process parameters, and descriptors are used that describe or affect the functioning of the studied natural object or geosystem. The most convenient for the study of dynamic and fairly complex natural geosystems are universal software packages built using simulation methods. The simulation model reveals such features of the modeled object as connections between components and their interdependence.

Illustrations are associated with such models using graphic images, which is one of the main advantages of such modeling. Visual modeling packages create an extremely user-friendly environment on a computer in which you can also create virtual parallel systems. Object-oriented modeling technologies make it possible to expand the limits of applicability and the area of their further use for geocological research. However, all metals have individual reactivity, especially mobile forms. They also have different efficiencies in terms of exchange reactions and transformations in the soil pool.

So, mobile zinc is characterized by a fairly effective interaction with all soil components. This indicates good solubility and rapid transformation of zinc in the soil environment. At the same time, the form of zinc intake into the soil has little effect on its migration properties. Therefore, zinc is likely to form several immobilized forms: specifically sorbed, chemically bound, and coordinated with organic matter fractions.

For nickel, the form of entry of the element into the contaminated soil is very important. In the case of nickel, the transformation of its oxides into extremely poorly soluble compounds α-Ni (OH)2 and / or Ni, Al-layered double hydroxides is possible. This is confirmed by the low degree of extraction of acid-soluble forms of this metal from soils contaminated with Ni oxides.

This means that the form of HM entering the soil during pollution can significantly affect the content of the mobile form, which determines the ability to interact with organic matter. This is partly reflected in the different pattern of distribution halos in the soil layer in Fig. 1-2 and the ability to enter into exchange processes and complexation with soil organic matter.

To visualize the processes of interaction of two HMs with organic matter, a three-dimensional computer model of the simultaneous distribution of mobile forms of Zn and Ni was obtained Fig. 4.
The wireframe map of the three-dimensional distribution of mobile forms of TM revealed the presence of two oppositely directed extrema. For Zn, a direct correlation was found between the content and the Corg concentration.

An inverse relationship is observed for mobile Ni. The obtained distribution pattern confirms the different mechanism of interaction of two HMs with the organic matter of the soil environment under specified conditions with increased alkalinity. It should also be noted that nickel in soils can form compounds with organic matter in the form of readily soluble chelates, which is practically unlikely for Zn.

In addition, clay minerals of soils most intensively fix chemical elements with a small ionic radius. For comparison, we can give different ionic radii for Zn-74 pm and for Ni-69 pm (100 picometer (pm) = 1 angstrom). Thus, the use of empirical modeling techniques and the resulting distribution halos quite adequately reflects the specificity of the chemical properties of mobile forms of HM — Zn and Ni, as well as the efficiency of their binding with soil organic matter.

The obtained maps of the distribution of mobile forms of heavy metals both in the zone of hazardous objects and outside the influence of the pollution source demonstrate the direction of migration flows in urban anthropogenic landscapes and their interdependent behavior. Unfortunately, such approaches are practically not used in assessing the ecological state of territories and in carrying out state environmental control. Outdated GOSTs and approved methodological guidelines do not allow changing the existing methods of analysis, which undoubtedly limits the understanding of the behavior of pollutants and the real state of soil geosystems.

It should be emphasized that information on the presence of organic matter in the soil layer and the interaction of metals with it is necessary for the development of an environmentally friendly method for neutralizing contaminated soils in the zone of hazardous objects and urbanized areas. The choice for reclamation of such territories in the zone of a hazardous facility as a gas station is very limited.

In particular, phytoremediation should not be used, since the drying up vegetative part of plants is very dangerous from a fire hazard point of view. However, it is the mobile water-soluble and exchangeable HM fractions that are biologically available forms of HM compounds in soils in the case of soil neutralization with the help of plants.

Therefore, the introduction of organic matter is the most acceptable way of immobilizing metals, however, taking into account the individual characteristics of their behavior in the soil.
5. Conclusion
On the basis of empirical simulation, the new results of the interdependent distribution of mobile forms of Zn and Ni were obtained. The use of Golden Software SURFER 8 made it possible to detect soil contamination halos laterally module - in the zone of a hazardous facility in the city. A three-dimensional frame model of the distribution of mobile forms of HM was obtained depending on the key soil parameter - Corg. The observed picture quite adequately reflects the specificity of their chemical properties and clearly demonstrates the different efficiency of binding of mobile forms of HMs with soil organic matter.

The proposed approach to geochemical modeling can be recommended as a methodological guide for identifying the features of behavior in the soil environment for other heavy metals. Such computer models also make it possible to predict the ecological state of disturbed soils for making environmental decisions, restoration measures, to support organizational decisions and contribute to the development of methods for modeling complex systems.

The results obtained also prove the need to change approaches to the ecological assessment of territories in the conditions of technogenesis and to revise the criteria for standardization based on general indicators.

Research has a promising development for the purpose of ecological diagnostics of geosystems. The developed approach makes it possible to obtain new geochemical patterns and associations of elements in technogenic landscapes, which contributes to the development of the fundamental foundations of geochemical science.

6. References
[1] Ibanez J J 2006 Future of soil science Wageningen: IUSS 60-62
[2] Crommentuijn T, Sijm D, Bruijn J, Hoop M, Leeuwen K, Plassche E 2000 Maximum permissible and negligible concentrations for metals and metalloids in the Netherlands, taking into account background concentrations Jornal Environmental Management Vol 60 121 – 143
[3] Ishchenko V 2017 Soil contamination by heavy metal mobile form near landfill International Journal Environment. Waste Management 20(1) 66 – 74
[4] Morin G, Ostergren J D, Juillot F, Ildefonse P, Calas G, Brown J E 1999 XAFS determination of the chemical form of lead in smelter-contaminated soils and mine tailings: Importance of adsorption process Am. Mineral V 84 420-434
[5] Mondal M K, Bhuivan S I, Franco D T 2001 Soil Salinity Reduction and Prediction of Salt Dynamics in the Coastal Ricelands of Bangladesh Agricultural Water Management Vol 47 9 23
[6] Vogel H-J, Bartke S, Daedlow K, Helming K, Kögel-Knabner I, Lang B, Rabot E, Russel D, Stößel B, Weller U, Wiesmeier M, Wollschläger U 2018 A systemic approach for modeling soil functions SOIL 4 83–92 https://doi.org/10.5194/soil-4-83-2018
[7] von Lützow M, Kögel-Knabner I, Ludwig B, Matzner E, Flessa H, Ekschmitt K, Guggenberger G, Marschner B, Kalbitz K 2008 Stabilization mechanisms of organic matter in four temperate soils: Development and application of a conceptual model J. Plant Nutrition and Soil Sci Vol 171 111-124
[8] Morin G, Juillot F, Casiot C, Bruneel O, Persone J-C, Elbaz-Poulhichet F, Leblanc M, Ildefonse P, Calas G 2003 Bacterial formation of tooeleite and mixed arsenic (III) or arsenic (V) – iron (III) gels in the Carnoules acid mine drainage France A XANES, XRD, fnd SEM study Environ. Sci. Technol Vol 37 1705-1712
[9] Sanderson J, Harris L D 2000 Landscape Ecology: A Top-Down Approach (Lewis Publishers, Boca Raton: Florida, USA) p 246
[10] Yüksel A, Akay A, Gundogan R 2008 Using ASTER Imagery in Land Use/cover Classification of Eastern Mediterranean Landscapes According to CORINE Land Cover Project Sensors 8 pp 1237–1251 https://doi.org/10.3390/s8021287
[11] Vogel H-J, Bartke S, Daedlow K, Helming K, Kögel-Knabner I, Lang B, Rabot E, Russell D, Stößel B, Weller U, Wiesmeier M, Wollschläger U 2018 A systemic approach for modeling soil functions 4 83–92 https://doi.org/10.5194/soil-4-83-2018
[12] Yang T, Liu Q, Chan L, Cao G 2007 Magnetic investigation of heavy metals contamination in urban topsoils around the East Lake Wuhan, China. Geophys. J. Int. Vol 171 603-612
[13] Zhang W X 2003 Nano scale iron particle for environmental remediation: an overview J. Nanopart Vol 5 323-332
[14] Scheckel K G, Scheinost A C, Ford R G, Sparks D L 2000 Stability of layered Ni hydroxide surface precipitates – A dissolutin kinetics study Geochim. Cosmochim. Acta Vol 64 2727-2735
[15] Schlegel M L, Manceau A, Charlet L, Chatteigner D, Hazemann J L 2001 Sorption of metal ions on clay minerals Nucleation and epitaxial growth of Zn phyllosilicate on the edges of hectorite. Geochim. Cosmochim. Acta Vol 65 4155-4170
[16] Roberts D R, Scheinost A C, Sparks D L 2002 Zink speciation in a smelter-contaminated soil profile using bulk and microscopic techniques Environ. Sci. Technol Vol 36 1742-1750
[17] Sarapulova G I, Fedotov K V 2018 Heavy metals migration decrease in the area of industrial facility for environmental safety The Collection of articles of the XXIX IMC-2018 International Congress Moscow: IPKON RAS 120-130
[18] Pils J R, Karathanasis A D, Mueller T G 2004 Concentration and distribution of six trace metals in northern Kentucky soils Soil Sediment Contam Vol 13 37-51
[19] Nowack B, Obrecht J-M, Schluep M, Schulin R, Hansmann W, Koppel V 2001 Elevated lead and zinc contents in remote alpine soils of the Swiss National Park J. Environ. Qual. Vol 30 919-926
[20] Karathanasis A D 2003 Mineral controls in colloidmediated transport of metals in soil environments Geochemical and Hydrological Reactivity of Heavy Metals in Soils Boca Raton.: Lewis Publishers p 360