Geoecological zoning of modern geological objects composed of technogenic soils. Distribution of Zn, Cu, Pb, Fe, Hg and As in technogenic dispersed soils and bottom sediments

I I Podlipskiy, S V Dubrova, P S Zelenkovskiy, S V Lebedev, O S Izosimova, E N Chernova, E M Nesterov and P I Egorov

1 Herzen State Pedagogical University of Russia, 48, Moika Emb., St. Petersburg, 191186, Russia
2 Saint Petersburg State University, 7/9 Universitetskaya Emb., St. Petersburg 199034, Russia

E-mail: podlipskiy@herzen.spb.ru

Abstract. The article presents a new methodology for the internal differentiation of technogenic objects (ash and slag dumps) based on ecological and geological studies of soils, bottom sediments, surface and underground waters, based on the allocation of three zones with various permissible types of nature management in their territory. The first zone (I) is the territory directly connected with the technogenic object (the bottom of the dump); the allocation of borders of the first kind is justified by the data of the cadastral division of land and the results of route surveys. The second zone (II) is the territory of the active manifestation of the impact of the object, which has a visual manifestation (the area of wind separation, the area of accumulation of solid surface runoff, the zone of drying or inhibition of the natural stand and growth), at the initial stages of the process of natural assimilation of exposure and/or at the initial stages of regression, first of all, phytocenosis. The third zone (III) represents the territory of active natural assimilation (general dispersion and/or concentration on natural geochemical barriers) of ash and slag material products (primarily, scattering flows of heavy metals and other pollutants). An analysis of the results of this work made it possible to specify the types of environmental protection measures that are carried out depending on the identified geochemical zones, the use of which—within the framework of projects of improvement and environmental monitoring of the sanitary protection zone—will significantly reduce the costs of nature users. The rationalization of the economic and legal components is associated with a decrease in the areas for a specific type of work, and all the activities of the nature user in the controlled territory.

1. Introduction

In accordance with the principles of ecological geology, dumps and landfills of industrial soils (municipal and industrial wastes) are an anthropogenically modified ecological and geological system, including the geological body of natural and technogenic genesis, underlying rocks and adjacent territories [1].

A separate problem is the zoning of such geological objects. Large-scale (zonal) division allows structuring the information on any objects, thereby simplifying the idea of patterns and reducing the amount of information for better presentation. Such a vision applies to all geological objects and their natural environment. The geochemistry of technogenic soils is such that the contrast of changes in the
concentration levels of chemical elements and substances from zone to zone is extremely high \[2–4\]. This fact is of great importance for compiling a methodological approach and assessing the migration of pollutants to existing natural ecosystems, highlighting priority areas in the study of geological objects of technogenesis and modeling processes occurring inside \[5–7\].

In this regard, a new methodology is proposed for the internal differentiation of anthropogenic objects, on the example of an ash and slag dump, based on ecological and geological studies of soils, bottom sediments, surface and underground waters, etc. their territories \[1\]:

- **first zone (I)** is directly connected with the technogenic object (the bottom of the dump). The allocation of borders of the first kind is justified by the data of the cadastral division of land and the results of route surveys.

- **second zone (II)** is the territory of the active manifestation of the impact of an object that has a visual manifestation (the area of wind separation, the area of accumulation of solid surface runoff, the zone of drying or inhibition of the natural stand and growth), located at the initial stages of the process of natural assimilation of impact and/or at the initial stages of regression, primarily phytocenosis. Region II is characterized by high concentration coefficients (more than 5) of the main typomorphic pollutants in the components of the natural environment. The identification of the boundaries of the second kind is associated with the results of route surveys, landscape, geobotanical, and soil mapping.

- **third zone (III)** represents the area of active natural assimilation (general dispersion and/or concentration on natural geochemical barriers) of ash and slag material products (primarily, scattering flows of heavy metal and other pollutants). This territory, as a whole, is characterized by low values of concentration coefficients (about 90% of the sample is lower than the background values). The identification of the boundaries of the third kind is based on the results of litho- and biogeochemical testing of soils and the most mobile components of the natural environment—air (spot testing on the main points, dust shooting, etc.) and water (surface and underground).

In total, all regions comprise the sanitary protection zone (SPZ) of the technogenic facility (ash dump refers to industrial facilities of class I with the size of the sanitary protection zone of 1000 m).

2. **Materials and methods**

The object of study is located in the north-east of Lake Ladoga in the city of Pitkyaranta (Republic of Karelia, Russia) and is a dump of ash and slag formed in the middle of the 19th century during the metallurgical “wet” processing of polymetallic ores from the deposits confined to the southern border of the Koyrino-Pitkaranta granite-gneiss domes (“Staroye rudnoye pole”, “Pitkyarskoye mestorozhdeniye”).

Ash and slag dump is an irregularly shaped body with dimensions of at least 150 × 250 m (about 0.5 km\(^2\)), with the thickness from 0.3 to 9 m and a volume of at least 3-3.5 × 10\(^6\) m\(^3\), located in the historical center of the city on the first coastal terrace of Pitkyaranta Bay of the Ladoga Lake. The slope of the relief (5-7°) is directed toward the coastline; the distance to the water edge during the low-water period is about 3-5 m. Ash and slag material on the day surface is a loose mass of brown and light brown colors, which slopes are exposed to active water and wind erosion. The boundaries of the dump (sole) are partially sod, hidden by personal plots and low-rise residential buildings.

This article generalizes and jointly analyses the research materials from 2003-2015 obtained by student teams under the guidance of teachers of the Department of Environmental Geology of St. Petersburg State University A.M. Belyaev and I.I Podlipsky.

Over more than 10 years of field and laboratory work in this territory, the following types of studies were carried out:

1. Lithogeochemical survey of the visible part of the dump and adjacent territories over the network with a step of 5 × 5 to 50 × 50 m using the “envelope” method from a depth of 0.0-0.1 and 0.0-0.2 m. The total number of selected and analyzed samples is more than 5 thousand pieces. The results of the analysis of the samples were used excluding the year of sampling. The analysis methods are X-ray fluorescence and atomic absorption for the content of Zn, Cu, Pb, Fe, Sr, Ti, V, Cr, Hg, As;
2. Sampling, analysis of the chemical composition of surface and ground (from wells and pits) waters. The total number of samples taken and analyzed is 14 pieces. The analysis method is atomic absorption for the content of Zn, Cu, Pb, Fe, Sr, Ti, V, Cr, Hg, As;

3. Evaluation of the composition of the forms found by the atomic absorption method of Zn, Cu, Pb, Fe, Hg and As in technogenic dumps by the method of sequential extraction (6 stages). The total number of samples taken and analyzed is 5 pieces;

4. Evaluation of the radial migration of pollutants in technogenic deposits over their entire thickness (6–8 m), by layer-by-layer sampling of combined samples of ash and slag material carried out during drilling operations. Sample preparation included standard methods for obtaining air-dried samples, methods of wet ashing. The analysis methods are X-ray fluorescence and atomic absorption for the content of Zn, Cu, Pb, Fe, Sr, Ti, V, Cr, Hg, As and other elements. The total number of samples taken and analyzed is more than 50 pieces;

5. Assessment of the particle size distribution of ash and slag material in dumps (areometric method for determining the particle size distribution of soils). The total number of samples taken and analyzed is 5 pieces.

The lithogeochemical matrix obtained by combining all the initial data of surface sampling for the entire period of survey work was divided into 3 samples, according to the developed author's approach, relating to three zones.

Each of the obtained samples of soil samples (zones I-III) at the first stage of data processing was subjected to statistical analysis, using the STATISTICA 10.1 software, using the “Basic Statistics and Tables” module and displaying stable estimates of mathematical expectation and scattering, as well as determining the presence of errors and outliers (both positive and negative) using the 3δ method and allowing to evaluate the basic statistical patterns.

After establishing and substantiating the mathematical significance of the differences in the samples (1-3), further mathematical processing was carried out using correlation and factor analysis. The latter was performed on the basis of the correlation matrix, by the method of principal components, followed by Varimax rotation. The critical value of the significance level is 5%.

To characterize the internal structure and homogeneity of the geological body of the ash and slag dump and the radial chemical composition, we used the data obtained as a result of drilling operations, granulometric studies of samples from different depths, and determination of mineral phases in industrial deposits (taken horizontally to the bottom of the dump) using the qualitative X-ray phase analysis.

In order to establish environmental hazard (determination of the category of ash and slag material pollution, the total pollution index (Zc) was calculated using background contents calculated taking into account the hazard class of the elements. The next step in determining the environmental hazard of ash and slag material is to establish the environmental hazard class by calculation method, based on the content of the main pollutants (heavy metals and metalloids).

3. Results and Discussion
The analysis of data on the composition of three samples (I-II-III) allowed establishing the following features (Figure 1):

- the small actual size of the “box” (the central part of the diagram, the sample part between 25 and 75% of the quartile) and the relatively long “upper whisker” (the degree of difference between the maximum value and the median and 50% of the sample), suggest a constant influx or excess availability of pollutant in the system (characteristic of all studied elements (Zn, Cu, As, and Pb), except Fe).

- an increase in the actual size of the “box” (reduction in the scatter of values, i.e. the difference between the maximum and minimum values) from zone I to zone III, indicates a decrease in the contrast of the anomaly and an increase in the homogeneity and homogeneity of the geochemical field, which is an indirect evidence of the assimilation of the geochemical effect exerted by the technogenic body.
An analysis of the correlation fields shows that the dependence between the variables (Cu-Zn, Zn-Pb, Cu-Pb) is close to linear and the allocation of hidden factors by the principal component method is possible.

To highlight the associations of chemical elements, methods of multivariate statistical analysis and, in particular, the factor analysis method were used. When selecting significant factors using the “scree” criterion, it was found that two factors are significant in assessing each of the samples.

Figure 1. The results of descriptive statistics of the three samples I-II-III and the separation of the contribution of various sources to the general geochemical field of the system “man-made dump – adjacent territories”

Based on the results of a factor analysis of the samples in three parts of the sanitary protection zone of a modern geological object composed of technogenic soil, a pattern was established consisting in the inclusion of natural elements in obviously technogenic associations (Zn-Pb-Cu) or the combination of technogenic with natural environment-forming elements (Pb-Fe).

According to the results of a study of the homogeneity of the internal composition of the industrial body of the ash and slag dump, we can conclude about a certain degree of stratigraphic homogeneity and the absence of visual signs of profile differentiation.

The radial geochemical structure of the geological body of the ash dump and underlying soils is a relatively contrast system (Figure 2):
• the surface peak (from 0-10 cm to 30-50 cm) can be associated with the beginning of the process of soil formation and accumulation of organic matter, which is a good adsorbent of heavy metals and metalloids [8, 9];
• the peak established in the sampling horizons from 65-70 cm to 100-110 cm may be due to the processes of glazing (radial migration of the fine solid phase) occurring in the territories of ash- and ash-and-slag dumps;
• the peak established in the sampling horizons from 130-150 cm to 350-400 cm is associated with a water-saturated horizon and possible secondary adsorption of mobile forms from overlying horizons [10], as evidenced by the analysis data (high values) of mobile forms of heavy metals in ash and slag material (acetate-ammonium buffer, pH 4.8) (Table 1).

![Figure 2. Scheme of radial differentiation, mg/kg](image)

Table 1. Mobile forms of heavy metals in ash and slag material, mg/l

| Indicator  | Fe  | Mn  | Cu  | Zn  | Pb  | Co  | Ni  | Cr  | Cd  |
|------------|-----|-----|-----|-----|-----|-----|-----|-----|-----|
| median     | 13.3| 0.22| 38.1| 3.60| 0.18| 0.012| 0.03| 0.03| 0.015|
| 25% quartile| 10.8| 0.20| 28.3| 1.80| 0.18| 0.011| 0.02| 0.02| 0.013|
| 75% quartile| 16.6| 0.28| 72.5| 15.43| 0.77| 0.018| 0.08| 0.04| 0.027|

4. Conclusion

According to the calculation of the hazard class of industrial soils, all samples of ash and slag material belong to III-IV hazard classes, which clearly indicates the need for remediation measures in the study area. The results of determining the hazard class of soil samples taken from different areas of the sanitary protection zone did not find a statistically significant difference, which can indicate the relative variability of this standardized technique. On the contrary, the results of calculating the total pollution index of soil samples showed a clear difference in its distribution and average values (Figure 3).

The analysis of the results of this work enabled the specification of the types of environmental protection measures depending on the identified geochemical zones, the use of which within the framework of landscaping and environmental monitoring of sanitary protection zones, will significantly reduce the costs of nature users. The rationalization of the economic and legal components is associated with a decrease in the areas for a specific type of work, the amount of land needed and a significant decrease in the workflow in the field of functional zoning of territories, that is, the main most difficult areas for the nature user (owner of the landfill site) in the sanitary protection zone (Figure 4).
Figure 3. Results of descriptive statistics of the distribution of $Z_C$ in SPZ zones (arbitrary units on the vertical axis)

Figure 4. Scheme of geochemical zoning of the territory of the SPZ at the object of study

Thus, according to our data, the approach to the internal differentiation of territories of industrial facilities and places of burial (placement) of household (municipal) and industrial waste developed by the authors has received a sufficient degree of justification for the rationality of its use on the basis of lithogeochemical survey data.
In the future, the authors plan to conduct a joint analysis of the already processed information and biogeochemical survey data carried out by accumulative bioindication using tissues and organs of plants (woody and herbaceous) and living organisms (annelids and arthropods). In addition, the analysis will use the results of a bio-indicator assessment of favorable conditions by bilateral symmetry methods, as well as data from biotesting of soil, soil and water quality by seed germination.

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