Environmental Assessment of the Toxic Effect of Slagheap on Soil Continuum

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Abstract. This article shows the study of the toxicological state of soils in the areas of anthropogenic impact of slag dump industrial waste of aluminum casting in the Oryol region. The data obtained indicate a high impact of slag dumps as a result of waste storage in the production of aluminum casting [3]. The inter-elemental relationship between the studied toxic metals shows that heavy metals can also have the same anthropogenic origin, regardless of the sources of their origin. The results of the pollution index prove the moderately high level of pollution of the study areas. A comprehensive assessment of the degree of degradation of light gray forest soils and their ecological resistance to natural processes and regimes, anthropogenic loads occurring in the soil profile [5] is shown. Analysis of the isotopic composition of heavy metals proves their obvious anthropogenic origin, including industrial emissions from an aluminum casting plant, exhaust gases derived from regular exposure to vehicles, as well as from dust storms. Studies are made of the effect of slag dumps on the environment, in particular, the effect on soil, water and plant cover. As a result of the research performed, the local impact of the slag dump on the adjacent territory and its pollution with a complex of heavy metals were revealed.

1. Introduction

As a result of the technogenic impact of slag dumps on the environment, there is a deterioration in the quality, disturbance, and alienation of lands, changes in the composition and properties of the geological environment, pollution of natural waters, the atmosphere, changes in the plant world and violation of the established hydro balance [3], [8]. Contamination of soil and plants with heavy metals has a detrimental effect on the growth and development of plants, the purification properties of water and food safety, this is becoming a global problem worldwide [10], [12]. In order to assess the spatial variations of soil contamination with heavy metals associated with regional land use [7], we collected soil samples for further quantification of heavy metals in the roadside, industrial, residential areas of the village of Bolshoe Dumchino, located in the Oryol Region of the Mtsensk District [17]. A
significant contribution to the amount of heavy metals entering the environment [15] is made by metallurgical enterprises, which are characterized by the presence of zones of maximum concentrations of heavy metals within a radius of up to five kilometers from the source of pollution and the expansion of areas of elevated concentrations of heavy metals to 20-50 km from pollution sources [11]. Every year, the problem with the formed and accumulated industrial and household waste becomes more acute [2].

It is known that heavy metals include chemical elements that have a density of more than 5 g/cm³ and an atomic mass of more than 40 g/mol [18]. The accumulation of heavy metals in the soil leads to an increase in their mobility by penetration into the deeper layers of the soil cover, as well as to the pollution of vegetation, the inhibition of biota and an increase in the content of heavy metals in groundwater [17], [18]. Despite a decrease in aerial emissions from industrial metallurgical enterprises and a decrease in the flow of pollutants into the soil by air, aerial emissions reach high levels, especially in industrial Asian countries, the USA, and Canada. The correlation between the content of heavy metals and the distance from the source of soil pollution located on the edges of highways and soils located around the slag dumps is obvious [4], [9]. Heavy metals exhibit high chemical activity in the soil, which leads to a slight degree of absorption by plants and ultimately threatens human health through the food chain. The general used pollution indices for toxic heavy metals in soils and sediments are defined in two main categories: single and integrated indices [3]. First, single methods include enrichment factor (EF), geoaccumulation index (Igeo) and pollution index (PI), which measure a single heavy metal and determine the background of a threshold pollution level. Second, integrated indices, such as the Integration Pollution Index (IPI), the Nemerow's Pollution Index (NPI) and the Risk Index (RI), apply to more than one metal and are an integration value of toxic heavy metal contamination for each testing of samples taken and also, can be compiled for each of the single indices. Measurement of the total amount of lead (Pb) in soil samples shows a general picture of the level of environmental pollution. The direct effect of heavy metals on the reaction of the soil environment [15] occurs due to the interaction of heavy metal compounds with water, which practically leads to a decrease in pH since heavy metal compounds are hydrolytically acidic [13]. Correlation analysis shows that the increase in lead content is associated with an increase in the content of mobile cadmium [1]. Currently, special attention is paid to the study of heavy metals in soils as the most dangerous pollutants, since their emissions are actively deposited in the surface layer of the soil cover. An analysis of literature data showed that when assessing soil contamination with heavy metals on various soil types, some types of biota become more informative [7], [20]. Some authors suggest that the toxicity of heavy metals is entirely due to the inhibition of many enzymes. The very effect of heavy metals on soil properties depends on the form of chemical compounds and the time from the moment of pollution to the study. Analysis of scientific publications also shows that indicators of the biochemical activity of the soil and the response of living organisms that inhabit the soil are used to characterize soils contaminated with toxic substances.

2. Problem statement

The main source of pollution is technogenic formations stored in slag dumps, characterized by significant concentrations of heavy metals causing mechanical and chemical pollution of the adjacent territories, with the highest amount of metals being detected in the upper soil layer. Slag dump Open JSC "Non-ferrous metals and alloys" (CMiS) operates from 1963 to 1994, consists of a dump of domain-containing aluminum slags [19]. The dump occupies an area of 9.9 hectares, the maximum excess over the natural relief of 44 m, in which the bulk material of small fractions of furnace slags is stored [19]. By chemical composition, slag wastes [16] consist of aluminum oxides (16.26%), silicon (4.9%), sodium, potassium chlorides [16]. The most potentially dangerous elements affecting the environment are heavy metals contained in slags as iron, copper, zinc, manganese [14].

The experience of monitoring around the slag dump allowed us to obtain a number of regularities [5], [7]. Slag dump affects the composition of atmospheric air and soil at a distance of 150-450 m, mainly in the direction of the prevailing winds [9].
In this regard, the aim of our work is to study the technogenic impact of the slag dump on the soil cover of its location: the village of Bolshoe Dumchino, Mtsensk District, Oryol Region.

3. Research questions and purpose of the study
The objectives of the study included:
1. To study the effect of the slag dump on light gray forest soils.
2. To assess the environmental state of the environment in the zone of influence of the slag dump.

4. Object and methods
The research area is the slag dump of the Mtsensk aluminum casting plant in the area of the village of Bolshoe Dumchino, the storage period for waste from 1963 to the present.

For the works, soil sampling points were laid. Samples were taken at a distance of 150 m from the source of pollution. Soils were sampled according to GOST 17.4.4.02 - 84 from a depth of 0–20 cm, with a mass of at least 1.5 kg each, taking into account wind rose and dispersion of suspended particles in a given area (Figure 1).

![Figure 1. Soil sampling points in the slag area.](image)

Investigations of the effect of the slag dump on the geochemical characteristics of landscapes made it possible to identify the distribution of pollutant metals in the soil cover and to assess the degree of accumulation of pollutants in the studied objects [20]. Proved a close relationship between the location of the source of pollutants, their characteristics, wind direction and fields of concentration of pollutants [10]. The determination of heavy metals in the soil was carried out by atomic absorption spectroscopy using an atomic absorption spectrometer with electrothermal atomization [21].

5. Result
The content of mobile forms of metals in samples of light gray forest soils in the zone of influence of the slag dump in the humus horizon of 0-20 cm at a distance of 150 m from the slag dump varies for cadmium in the range of 0.15 to 2.18 mg/kg [3]. The greatest accumulation of cadmium is observed in the east direction at point No. 4, where its amount reaches 2.18 mg/kg (Figure 2).

![Figure 2. Cadmium content in soils.](image)
Research has shown that the content of cadmium in the soil varies within 0.15 mg/kg - 1.71 mg/kg. The greatest accumulation of cadmium is observed in the east direction at point No. 4, where its amount reaches 2.18 mg/kg. The manganese content in the soil ranges from 7.7 mg/kg to 188.1 mg/kg (Figure 3).

![Figure 3. Manganese content in soils.](image)

The greatest concentration of this metal is noted on a large area of the territory adjacent to the slag dump in the northeast and southeast directions (points No. 3, 4, 5). In the upper soil horizon, the amount of accumulated manganese reaches 188 mg/kg at point 4, at points 3 and 5 its amount is 154 mg/kg and 104 mg/kg, respectively.

The change in the nickel content presented in Figure 4, from which it can be seen that its amount varies between 1.15–9.21 mg/kg, and the highest values are set in the north-east direction at the point No. 3-9.21 mg/kg and the south-east direction at points No. 4-8.4 mg/kg and No. 5-7.83 mg/kg (Figure 4).

![Figure 4. Nickel content in soils.](image)

The change in lead content in the soil ranges from 0.64 to 149.81 mg/kg. The maximum lead concentration is noted in the south-east direction at point No. 5 and reaches 150.0 mg/kg (Figure 5).

![Figure 5. Lead content in soils.](image)

The zinc content in the studied area in the humus horizon of 0-20 cm of light gray forest soil at a distance of 150 m ranges from 2.59 to 197.57 mg/kg. The greatest accumulation of zinc is observed in the north-east direction of the 150-meter zone at point No. 3 (197.57 mg/kg), while the minimum amounts are set at points No. 1,9,10 in the north and north-west directions from 2.59 up to 12 mg/kg (Figure 6).
Studies have shown that the copper content in the soil varies from 0.17 mg/kg to 17.47 mg/kg in the zone of influence of the slag dump. The highest concentration of this metal is shown in the south-east direction at point No. 5, at points No. 4, 6, 7 and 8 the amount of copper in the soil decreases to 13.1 mg/kg, 12.2 mg/kg, 11.1 mg/kg and 9 mg/kg (point number 8). At points 1, 9, and 10, the smallest quantities of mobile copper are installed (Figure 7).

The maximum contribution to the mass of pollutants of the upper humus horizon of light gray forest soil is made by zinc (42.6%), followed by manganese (37%) and lead (13%) and copper (6%). The degree of soil contamination was estimated by the values of the concentration coefficient of pollutants (heavy metals) in soil $K_c = C_{me} / C_{MCP}$, where $C_{me}$ is the average metal concentration in soil mg/kg; $C_{MCP}$ – the maximum permissible concentration of polluting heavy metals in accordance with GN 2.1.7.2014-06. The total indicator of chemical pollution of the humus horizon of light gray forest soil with heavy metals is calculated by the value of:

$$Z_c = K_1 + K_2 + \ldots + K_n - (n-1)$$  \hspace{1cm} (1)

where $n$ is the number of considered heavy metals (table 1).

The total coefficient of chemical pollution of the soil for the upper humus horizon of light gray forest soil varies within 1.33-11.29, which characterizes the permissible or moderate degree of soil contamination. The elements of the magnitude of the excess over the values of the maximum permissible concentrations of their content in the soil form the following row: Zn > Pb > Cu > Ni > Cd.

A significant excess of MPC is established for such metals as lead, the content of which exceeds the MPC by 1.17-3.83 times, the excess of the maximum permissible concentration is also established for zinc in soil samples No. 2 and No. 3, the value of which concentration coefficient fluctuated within 2.19 (sample No. 2) and 5.59 (sample No. 3). The MPC excess was also established for such a metal as copper, whose content in soil sample No. 1 was 1.16 times the maximum permissible concentration, and in soil sample No. 3 it was 2.57 times. The content of mobile manganese does not exceed the maximum permissible level of its concentration in the soil and is significantly below this level of accumulation in the soil.
Table 1. Coefficients of heavy metal concentration in the upper humus layer (0-20 cm) in light gray forest soil.

| Metal  | Sample №1 | Sample №2 | Sample №3 | MPC |
|--------|------------|------------|------------|-----|
| Cadmium| 0,21       | 2,18       | 0,65       | 1,0 |
| Lead   | 1,17       | 1,45       | 3,83       | 6,0 |
| Nickel | 0,62       | 0,42       | 2,3        | 4,0 |
| Zinc   | 0,93       | 2,19       | 5,59       | 23,0|
| Copper | 1,16       | 0,92       | 2,57       | 3,0 |
| Manganese| 0,17     | 0,11       | 0,51       | 140,0|
| Zc     | 1,33       | 3,82       | 11,29      |     |

For mobile forms of cadmium and nickel, it is shown that the maximum permissible level of their quantity in the humus layer of light gray forest soil is 2.2 times higher for cadmium (sample No. 2) and 2.3 times for nickel (sample No. 3).

The formation of the chemical composition of surface waters occurs as a result of leaching processes, ionic water exchange, and the vital activity of organisms. Water plays a major role in the redistribution of chemical elements in the earth’s crust. The highest content in waters falls on the following elements [8]: Cl, S, C, Si, N, O, H, K, Na, Ca, Mg, Fe, Al [8].

The creation of a slag dump led to a change in the hydrogeological and hydrological conditions on the occupied area of the land plot [13]. Slag dumping has violated surface runoff, which has led to waterlogging in the surrounding area. Atmospheric precipitation infiltrating through the body of the dump is saturated with water-soluble components and pollutes both surface and ground waters in the absence of impervious protection [11]. Conducted studies of water samples taken from a surface water body located in the zone of influence of the slag dump indicate a change in the chemical composition of surface water under the influence of pollutants entering with surface and underground runoff. The calculation of the share of the water-soluble slag phase showed that the content of strontium (22 times), sodium (9 times), chlorides (8.3 times), ammonia (6 times), manganese (1.6 times) exceeds their maximum allowable concentrations in surface waters. The total mineralization of water exceeds the maximum permissible level by 3.3 times, which makes it possible to consider such water brine according to OA Alyokin and moderately hard, which is caused by the presence of sodium hydroxide, bicarbonate and sodium carbonate, calcium and magnesium in waters [13].

Studies of the effect of the slag dump on the environment made it possible to identify the distribution patterns of polluting metals in the soil cover and to assess the degree of accumulation of pollutants in the objects under study. Proved a close relationship between the remote location of the source of pollutants and their characteristics with the fields of concentration of pollutants in the soil (Table 2).

Table 2. The content of mobile and gross forms of heavy metals in light gray forest soils (0-20 cm) in the zone of influence of the slag dump.

| Distance, m | Cd   | Cu   | Zn   | Pb   |
|-------------|------|------|------|------|
| 20          | 0,61*| 47,45| 45,30| 14,06|
|             | 1,45**| 209,95| 136,61| 97,85|
| 150         | 0,18 | 4,0  | 6,95 | 3,31 |
|             | 0,71 | 56,65| 65,45| 20,81|
| 300         | 0,07 | 4,71 | 4,65 | 3,69 |
|             | 0,29 | 46,45| 51,95| 14,90|
| 450         | 0,05 | 1,52 | 1,85 | 1,12 |
|             | 0,18 | 21,95| 35,35| 7,02 |
| MPC         | 1,0  | 3,0  | 23   | 6,0  |
|             | 0,5  | 55   | 45   | 30   |

* -mobile forms HM; ** - gross forms of HM
6. Conclusion
The content of mobile forms of metals in soil samples in the zone of influence of the slag dump on the humus horizon of the light gray forest soil exceeds the maximum permissible level for copper, zinc, and lead in close proximity (20 m) to the slag dump, so for copper this excess was 15, 8 MPC, for zinc 1.9 MPC, for lead 2.3 MPC. With increasing remoteness of the experimental sites from the slag dump, the content of mobile forms of the studied metals in the upper humus layer of light gray forest soil decreases sharply and does not exceed the value of the maximum permissible level for cadmium, zinc, and lead. The exception is the content of mobile copper, the amount of this metal is 1.3-1.6 times the maximum permissible concentration at experimental sites, remote from the slag dump by 150 and 300 meters (Table 2).

Analysis of the distribution of gross forms of heavy metals [7, 22] in the humus horizon of light gray forest soil at different distances from the slag dump showed that the content of cadmium, copper, zinc, and lead exceeds the maximum allowable level in the immediate vicinity of the studied soil areas (20th) to the slag dump, for example, the amount of gross cadmium was 1.45 mg/kg, and the total zinc content (136.6 mg/kg) was 3 times higher than the MPC, the amount of gross copper exceeded the maximum permissible level-up to 3.8 MPC, and the zinc content exceeded MPC 3.3 times.

At the same time, with the distance from the source of pollution, the gross amount of heavy metals in the humus layer of light-gray forest soil decreased almost 2 times in cadmium, 3.7 times in copper, the amount of zinc decreased almost 2.1 times and exceeded MPC 1.5 times. The amount of gross lead decreased by 4.7 times in comparison with the amount of the studied metal in the soil in close proximity to the slag dump and did not exceed the MAC. As a result of our research, the effect of slag wastes [16] on the spatial contamination of soils with heavy metals has been shown, which helps to identify the most efficient landscaping methods for phytoremediation of soils.

According to the results of monitoring studies, the complex impact of the slag dump on the natural environment, manifested in the dust load on the adjacent territories, pollution of the soil, surface and ground waters with heavy metals and having a negative impact on human health, has been revealed.

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