Heavy Metal Contamination of Urban Soil in Novosibirsk

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Abstract. This paper focuses on the problem of urban soil contamination with heavy metals in Novosibirsk city. The concentrations of mobile forms of heavy metals in soils of district of Novosibirsk affected by a non-ferrous metallurgy plant (Novosibirsk Tin Plant) were assessed. Soil samples were taken at 9 sites. Flame atomic absorption spectrometry and inductively coupled plasma mass spectrometry were employed for chemical analysis of the heavy metal contents. The study demonstrated that the maximum permissible concentrations (MPCs) for arsenic, lead, nickel, cadmium, copper, zinc and chromium were exceeded in the analysed samples and the concentration of mercury is in normal levels. The concentration of heavy metals decreased with increasing distance from the plant. According to the integrated pollution index soil contamination is classified as extremely hazardous.

1. Introduction
The rapidly developing industries, as well as worldwide urbanization and industrialization, have made the problem of environmental pollution with heavy metals (HMs) global [1]. Heavy metals are the most hazardous anthropogenic inorganic xenobiotics [2]. After being introduced into the environment, they act as toxicants and environmental toxicants. Some heavy metals and metalloids can be hyperaccumulated and cause mutagenic, teratogenic, and carcinogenic effects [3]. According to the data reported by the International Agency for Research on Cancer (IARC) operating under the auspices of the World Health Organization (WHO), arsenic and arsenic inorganic compounds, cadmium and cadmium compounds, nickel compounds, chromium (IV) compounds are classified as group 1 carcinogens (agents carcinogenic to humans); lead inorganic compounds and metallic nickel are classified as group 2B carcinogens (possibly carcinogenic to humans).

Pollutant concentration in landscape components is one of indicators of the technogenic impact on the environment. Urban soils undergo especially significant contamination. Soils are the main adsorbents for heavy metals introduced into the environment as a result of anthropogenic activities [4]. Unlike organic pollutants, heavy metals do not degrade but are converted from one form to another, so their contents in landscape components increase, thus forming secondary dissemination areas of elements that have been introduced into the soils.

Non-ferrous metallurgy enterprises are the major source of technogenic environmental pollution with heavy metals in industrial regions [5]. In this case, the main concern is that in the cities with multiple industries, the environment is polluted with a number of elements that can have a synergistic effect on the human body. Additivity or potentiation of the effects is especially unfavorable. The problem of environmental contamination with heavy metals is quite relevant in most Russian cities [6]. The mining industry and non-ferrous metallurgy enterprises are the main sources of heavy metals.
Novosibirsk Tin Plant (NTP) is a large enterprise having a technogenic effect on the environment in the city of Novosibirsk. This plant has been operating since 1942 and producing high-purity tin metal, babbitt alloys, and alloys based on tin, lead, copper, and antimony. The employed manufacturing process, imperfect waste treatment systems, and inadequate tailing disposal procedures have led to large-scale pollution of the surrounding areas. Environmental contamination with heavy metals primarily occurs as they are emitted into the atmosphere during high-temperature manufacturing processes and combustion of mineral fuels. Large amounts of tailings have been accumulated on the territory occupied by the plant; heavy metal compounds contained in them can be disseminated in air and leached by rainfall, thus causing soil contamination.

Earlier studies focused on aerosol pollution of the atmosphere [7] and snow cover [8] near the NTP. The gross contents of heavy metals in soil affected by the plant were analyzed [9]. However, because of the buffering capacity of soils, the gross content of heavy metals does not provide adequate information for the actual risk of contamination. Heavy metals can be accumulated by plants and move through food chain, thus exhibiting toxic and carcinogenic effects on the living organisms, which makes it necessary to identify mobile forms of heavy metals [10]. An analysis of the contents of mobile forms of heavy metals allows one to assess the bioavailability and the probability of element migration in soil [11].

Soil condition needs to be regularly monitored because of the increasing technogenic load on environmental objects, development of urban infrastructure, urbanization, and population growth. Due to the decreased output of the NTP and modernization of waste treatment systems, the enterprise hazard class has been lowered and hence the sanitary protection zone has been reduced. As a result, from a legal viewpoint, residential construction is now allowed on the area that had been affected by the NTP for a long time. Intensive construction of multi-storey residential buildings currently takes place within the adjacent area. Another significant aspect demonstrating that environmental evaluation of soil condition needs to be performed is that a recreactional area and garden plots reside within the territory under study. The latter fact indicates that concentrations of mobile forms of heavy metals need to be determined, since consuming crops grown in soils contaminated with heavy metals (and, therefore, containing them) causes irreversible changes in the human body (the carcinogenic, mutagenic, and teratogenic effects).

Hence, it is evident that assessment of mobile forms of heavy metals in the areas surrounding the NTP is not only relevant, but highly needed as well.

The objective of this study was to perform an environmental assessment of the levels of soil contamination with mobile forms of heavy metals in the areas affected by a non-ferrous metallurgy enterprise, the Novosibirsk Tin Plant.

2. Materials and methods

2.1. Soil sampling

Nine sample plots were selected within the area affected by the NTP northeastward from the plant so as to embrace all types of urban zones in this district: the industrial, residential, and recreational ones. Sampling was performed in September, soil samples were collected on the same day under identical conditions. According to the standard, test sites must be selected taking into account the direction of the wind. Terrain is another significant factor. In this area, the height of the terrain decreases as it approaches the river Ob. Consequently, heavy metals in a mobile form, being in the form of free ions in the soil solution, migrate and leach towards a decrease in the relief. Based on these two factors, the north-east direction was chosen.

The samples were collected, treated, and stored in compliance with the requirements of the current state standard of the Russian Federation (GOST 17.4.4.02-2017).

In compliance with the requirements of the state standard, soil samples were collected layer-wise using the "envelope" method from depths of 0-20 cm. Incremental sampling was conducted using a plastic shovel to avoid recontamination of the samples.
Soil samples collected from the mouth of the Yeltsovka River (54.443188 N, 82.308552 E) were used as controls. This point is significantly remote from any industrial and agricultural enterprise. Samples of soil, water, or air unexposed to technogenic factors are often collected at this location in environmental chemistry experiments [12]. The background content of mobile forms of heavy metals in control soil samples is given in table 1. Regional background concentrations of the analyzed elements, with the exception of Ni, do not exceed the MPC.

The collected samples were air-dried at laboratory room ambient temperature and humidity. At the next step, the sample was pounded with a pestle in a mortar until a homogeneous state and sieved through a 1 mm nylon mesh.

2.2. Analytical methods

Chemical analysis was performed in the accredited chemical laboratory of the Institute of Solid State Chemistry and Mechanochemistry, SB RAS.

The content of mobile forms of heavy metals was determined by inductively coupled argon plasma mass spectrometry (ICP-MS) on an Agilent 7500a mass spectrometer made in Japan and by atomic absorption on an AA-280 FS spectrometer made in Australia in accordance with the PND F 16.2.2:2.3.71-2011. For each experimental point, three parallel measurements were carried out, the content of elements in the sample was calculated from the mean value.

Since the instruments are designed for the analysis of liquid samples, the solid samples were brought into solution. The mobile forms of the elements were extracted from the tested samples with 1 M solution of nitric acid of special purity grade.

Also during the study, some soil characteristics were identified that affect the mobility of heavy metals. These include the content of organic matter, the reaction of the environment and the water regime of the soil. The percentage of organic matter was determined by calcining samples of soils in a muffle furnace in accordance with GOST 27784-88, the pH value of soils was determined by the electrometric method in accordance with GOST 26423-85. Soil moisture was determined by drying samples in a drying oven to constant weight in accordance with GOST 5180-2015.

The level of soil contamination was assessed by comparing the contents of mobile forms of heavy metals in the test samples to the maximum permissible concentrations (MPCs) in compliance with the Sanitary and Hygienic Standard (GN 2.1.7.2041-06).

The concentration coefficients of a chemical substance $K_c$ were calculated to perform environmental assessment of the level of chemical pollution. When soil was contaminated with several heavy metals, the level of contamination should be assessed according to the integrated pollution index $Z_c$.

The concentration coefficient of a chemical substance $K_c$ is defined as the ratio between the actual concentration of an element in the sample under analysis and the background concentration of this element.

The integrated pollution index $Z_c$ is calculated using the formula:

$$Z_c = \sum_{i=1}^{n} K_c - (n-1)$$

where $n$ is the number of contaminants taken into account.

According to MU 2.1.7.730-99, 4 degrees of chemical soil contamination are distinguished depending on the values of the total pollution index $Z_c$: permissible ($Z_c < 16$), moderately hazardous ($16 < Z_c < 32$), hazardous ($32 < Z_c < 128$), extremely dangerous ($Z_c$ over 128).

Mathematical and statistical processing of the obtained data was carried out using the Microsoft Excel program and included the calculation of the arithmetic mean, standard deviation and other statistical parameters.
3. Result and discussion
The soils being analyzed have a neutral, weakly alkaline, and alkaline reaction, their pH ranges from 6.9 to 8.5. In neutral soils (pH 6.6-7.0), As and Zn compounds are mobile. With increasing pH, anion-forming elements (Cr) become mobile. In the acidic reaction of soils, the mobility of cation-forming metals increases (Zn, Cu, Pb) [13-21].

The accumulation of mobile forms of elements depends on the water regime of the soil, which is characterized by moisture. The humidity of the samples under study varies within 6-23%. This value indicates that the soil is characterized by a non-flushing regime. Under these conditions, HMs will accumulate more than in soils with a leaching regime, and, therefore, the proportion of potentially mobile HMs increases [14].

The solid phase of the soil consists of an organic and a mineral part. The high content of organic matter in the soil allows the formation of complex compounds with heavy metals, which are less accessible to plants. The percentage of the organic part of the studied soil is in the range of 10-29%. This means that the risk of accumulation of an excessive amount of mobile forms of elements in plants is higher than in soils with a high content of organic matter.

Table 1. Background concentration of mobile forms of heavy metals in control soil samples in Novosibirsk (number of control samples – 5, number of parallel measurements – 3).

| Element | Background concentration of mobile forms of HMs (mg/kg) |
|---------|--------------------------------------------------------|
| As      | 0.98±0.49                                             |
| Pb      | 3.15±1.13                                             |
| Zn      | 8.67±3.81                                             |
| Ni      | 5.20±2.18                                             |
| Cu      | 2.05±0.86                                             |

Comparison of the results of the studies with the maximum permissible concentrations provided in the Sanitary Regulations and Norms showed that the MPC values were exceeded for Cu, Ni, Cr, Pb, Zn and As; concentrations of Cd and Hg don’t exceed the MPC values. Thus soil contamination by HM in the NTP area is polyelemental. Heavy metals concentrations and MPC are given in table 2.

Table 2. Concentration of mobile forms of heavy metals in soil of Novosibirsk and MPC value.

| distance from the NTP (km) | concentration of Pb (mg/kg) | Concentration of As (mg/kg) | Concentration of Cd (mg/kg) | Concentration of Cu (mg/kg) | Concentration of Zn (mg/kg) | Concentration of Cr (mg/kg) | Concentration of Ni (mg/kg) |
|---------------------------|-------------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|-----------------------------|
|                           | 108.6±30.4                   | 153.6±21.5                  | 1.91±0.57                   | 73.8±22.1                   | 95.7±42.1                   | 44.2±25.7                   | 48.3±16.4                   |
|                           | ±27.9                        | ±21.5                      | ±0.57                       | ±25.1                       | ±36.1                       | ±25.7                       | ±23.8                       |
|                           | 59.8±21.5                    | 130.3±18.2                 | 1.26±0.38                   | 52.8±15.8                   | 112.0±58.9                  | 40.1±23.3                   | 48.3±14.2                   |
|                           | ±38.8±14.0                   | ±28.7                      | ±0.13                       | ±15.8                       | ±29.1                       | ±15.5                       | ±14.2                       |
|                           | 36.7±13.2                    | 24.4±1.4                   | 0.28±0.13                   | 32.3±9.7                    | 37.9±16.7                   | 41.8±18.4                   | 41.9±14.2                   |
|                           | ±29.4±10.6                   | ±1.4                       | ±0.25                       | ±7.5                        | ±16.7                       | ±8.2                        | ±12.0                       |
|                           | 29.4±10.6                    | 12.2±4.7                   | 0.27±0.14                   | 34.8±10.4                   | 27.3±8.2                    | 24.4±10.7                   | 35.4±12.0                   |
|                           | ±11.5±0.06                   | ±4.7                       | ±0.14                       | ±8.2                        | ±8.2                       | ±10.7                       | ±12.0                       |
|                           | 5.8±2.2                      |                            |                            |                            |                            |                            |                            |
|                           | MPC = 6.0 mg/kg              | MPC = 10.0 mg/kg           | MPC = 2.0 mg/kg             | MPC = 3.0 mg/kg             | MPC = 23.0 mg/kg            | MPC = 6.0 mg/kg             | MPC = 4.0 mg/kg             |
|                           | 19.1±0.7                     |                            |                            |                            |                            |                            |                            |

MPC = maximum permissible concentration.
Based on the totality of all the above soil factors in the industrial region of Novosibirsk, it can be concluded that the prerequisites for the accumulation of HMs in the soil have been created.

To determine the dependence of HMs concentrations on the distance of sampling points relative to the NTP, the correlation coefficients were calculated: Cu – 0.92; As – 0.8; Pb – 0.79; Zn – 0.51; Ni – 0.28; Cr – 0.18. These values confirm the fact that the NTP pollutes the adjacent territory with Cu, As, Pb, Zn. Their concentration decreases with distance from the enterprise.

The concentration coefficients calculated from the experimentally obtained data for each element: As – 54.3, Zn – 23.2, Cu – 21.9, Pb – 20.1, Ni – 7.8, Cr – 7.7.

The integrated pollution index \( Z_c \) for the area under study is equal to 130, corresponding to the class of extremely hazardous soil contamination.

4. Conclusion

Soil contamination in the industrial district of Novosibirsk affected by Novosibirsk Tin Plant, a non-ferrous metallurgy enterprise, was found to be polyelemental. The concentrations of mobile forms of Cr, Ni, Pb, Cu, Zn, and As are higher than the maximum permissible concentration (MPC) values specified in hygiene regulations within the entire area under study.

Although it is impossible to predict the trends in spatial distribution of heavy metals in the large industrial district without performing multi-year assessment of the activity of industrial enterprises, the resulting correlation ratios between concentrations of mobile forms of heavy metals and the distance between sampling sites and the plant demonstrate that the Novosibirsk Tin Plant affects the degree of soil contamination with such elements as Cu, Pb, and As.

According to the specified sanitary standards of the Russian Federation, the integrated index of soil contamination with heavy metals gives grounds for classifying these soils as ones subjected to extremely hazardous contamination.

The contamination with mobile forms of heavy metals in the garden plots within this district is especially hazardous, since this very form of heavy metals is accumulated by plants and moves through food webs. The content of arsenic, a group 1 carcinogen recognized by the WHO, is 15-fold higher than its MPC. The contents of group 2 carcinogens, nickel and lead, reach values 14-fold and 32-fold higher than their MPCs, respectively.

The contamination with heavy metals revealed in the industrial area indicates that measures for remediating and recultivating the contaminated soil need to be urgently elaborated.

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