UDC 504.064.2, 631.42

DOI: 10.15372/CSD20202560

Analysis of the Content of Mobile Forms of Heavy Metals in Soil in the Areas Affected by the Novosibirsk Tin Plant

S. S. SHATSKAYA[1], A. Y. KRASOVSKAYA[2], I. V. STOROZHKO[2], E. A. UDALTSOV[2]

[1]*Institute of Solid State Chemistry and Mechanochemistry, Siberian Branch, Russian Academy of Sciences, Novosibirsk, Russia*

E-mail: lana46@ngs.ru

[2]*Novosibirsk State Technical University, Novosibirsk, Russia*

(Received February 26, 2020; revised July 20, 2020)

Abstract

This work deals with the study of the problem of soil contamination with heavy metals in a large city. The content of mobile forms of heavy metals was determined in the soils of the industrial zone in the Kirovskiy region of Novosibirsk at the territory affected by the metallurgical enterprise – Novosibirsk tin plant. Chemical analysis was performed by means of inductively coupled plasma mass spectrometry and atomic absorption. It is shown that the maximum permissible concentrations (MPC) of the following heavy metals are exceeded in the samples under analysis: Cr, Ni, Zn, Pb, Cu. With an increase in the distance from the plant, the content of heavy metals decreases, but the permissible concentrations are exceeded even in the area of natural parkland. To calculate the accumulation of the mobile forms of heavy metals in the soil of the industrial zone near the plant, the MPC value for As was accepted to be equal to the maximum permissible excess (MPE). The sequence of accumulation of the mobile forms of heavy metals in the soil of industrial zone near the plant was formed according to the calculated concentration coefficients: Cr < Ni < Zn < Pb < Cu < As. The category of soil contamination is characterized according to the total pollution index as dangerous.

Keywords: heavy metals, ecotoxicants, accumulation, migration in the soil

INTRODUCTION

Impetuous development of industrial activities, ubiquitous urbanization and industrialization make the problem of soil pollution with heavy metals (HM) in Russia increasing from year to year [1–4].

Heavy metals are the most dangerous inorganic xenobiotics of anthropogenic origin [5]. Heavy metals are dangerous because they do not undergo degradation but only get transformed from one compound to another. Arriving into the soil, HM are accumulated in it and behave as ecotoxicants; they are able to be transferred along food chains into human organism [6]. In addition to the direct toxic effect, some HM may cause carcinogenic, mutagenic and teratogenic effects [7–9]. According to the data of the International Agency for Research on Cancer working under the control of the World Health Organization (WHO), arsenic, cadmium and its compounds are classified as carcinogens of group 1 (carcinogenic for humans); lead and nickel are carcinogens of group 2 (possible carcinogens for humans).

The mining industry and the enterprises of nonferrous metallurgy belong to the major sources of HM entering the environment [10–12]. A large LCC Novosibirsk Tin Plant (NTP) produces a technogenic effect on environmental objects in Novosibirsk. The plant operates since 1942 manufacturing tin, babbit and alloys based on tin, lead, copper and antimony. The major achievement of the plant is the production of super-pure tin (99.9999 %).

The nature of the technological process at NTP, imperfect purification systems and unreasonable utilization of the wastes from concentrating caused large-scale pollution of the adjacent territory. To determine the main substances entering the environment, analysis of the technological process of tin production was carried out [13]. The technological scheme includes the following stages: recovery of tin concentrates, roasting, reductive fusion, refining. The production of tin involves the release of a number of toxic substances: sulphur oxides, arsenic-containing compounds, lead, copper, zinc and iron-containing compounds. The major route along which heavy metals enter the environment is their emission into the atmosphere from high-temperature technological processes. At the same time, large amounts of wastes from concentrating have been accumulated at the territory occupied by the plant. The compounds of HM that are present in these wastes may be carried with the wind over long distances and get leached by atmospheric precipitation thus producing soli pollution.

The problem of the pollution of territory adjacent to NTP was considered previously: the aerosol pollution of air (2002) [14] and snow cover (2013) [15] was investigated, the overall HM content in the soil in the zone affected by the plant was determined (2004) [16]. However, due to the buffer capacity of the soil, the total HM content is not an informative parameter of the presence of real pollution danger. The most dangerous consequences for humans are connected with the presence of mobile forms of elements in soil [17, 18]. Analysis of the content of mobile HM forms allows evaluating biological availability, the possibility of element migration in soil and leaching into other media (ground and surface waters).

The necessity to study soils for the content of the mobile forms of HM in the Kirovskiy region of Novosibirsk is due to the fact that the territory under consideration hosts garden plots and recreation zone – Bugrinskaya Roshcha park for culture and leisure. Intense multistorey housing construction is carried out at a distance of 1 km from NTP. It is also necessary to take into account the fact that it is planned to move the industrial facilities of NTP out of the territory of the city, and the territory occupied today by the plant will be recultivated and stage-by-stage repurposed to social, business, trade, industrial construction [19].

The goal of the present work was to provide ecological evaluation of the level of soil pollution with HM in the mobile form in the zone affected by the enterprise of nonferrous metallurgy – NTP.

EXPERIMENTAL

Soil sampling

The Novosibirsk Tin Plant is one of the most powerful sources of the technogenic pollution of environment in the Kirovskiy District. We chose 9 test grounds at the territory affected by the plant. The test grounds were located to the north-east from the plant so that all urban zones could be involved: industrial, residential, and recreation. One soil sample was taken in the southern direction from the plant to evaluate the approximate level of territory pollution in the direction that was not the subject of investigation. As a result of dense urban built-up environment, the major part of soil is under the asphalt, which makes it impossible to collect soil samples at definite intervals from NTP.

Soil sampling, treatment and storage were carried out according to the requirements of the interstate standard GOST 17.4.4.02-2017, according to which test grounds were aligned with the vectors of wind direction frequencies. The dominating wind directions in Novosibirsk are from south and south-west [20]. The north-eastern direction from the industrial ground was chosen for investigation because it is this direction along which the new multistorey residential buildings are being constructed and garden plots are situated, where the crops contaminated with heavy metals are grown.

Another substantial factor that affected the choice of the north-eastern direction to study the degree of soil pollution is the relief. The altitude decreases while the Ob river is approached. Therefore, HM in the mobile form, namely in the form of ions in the soil solution, migrate and are leached towards the decrease in altitude.

The location of sampling sites, the diagram of wind frequencies (the wind rose) for the years 1966–2018 are shown in Fig. 1. The point of the zero wind force is placed at the chimney of NTP.

Soil was sampled in September 2018. According to the requirements of GOST 17.4.4.02-2017, soil samples were collected from test grounds 1 × 1 m

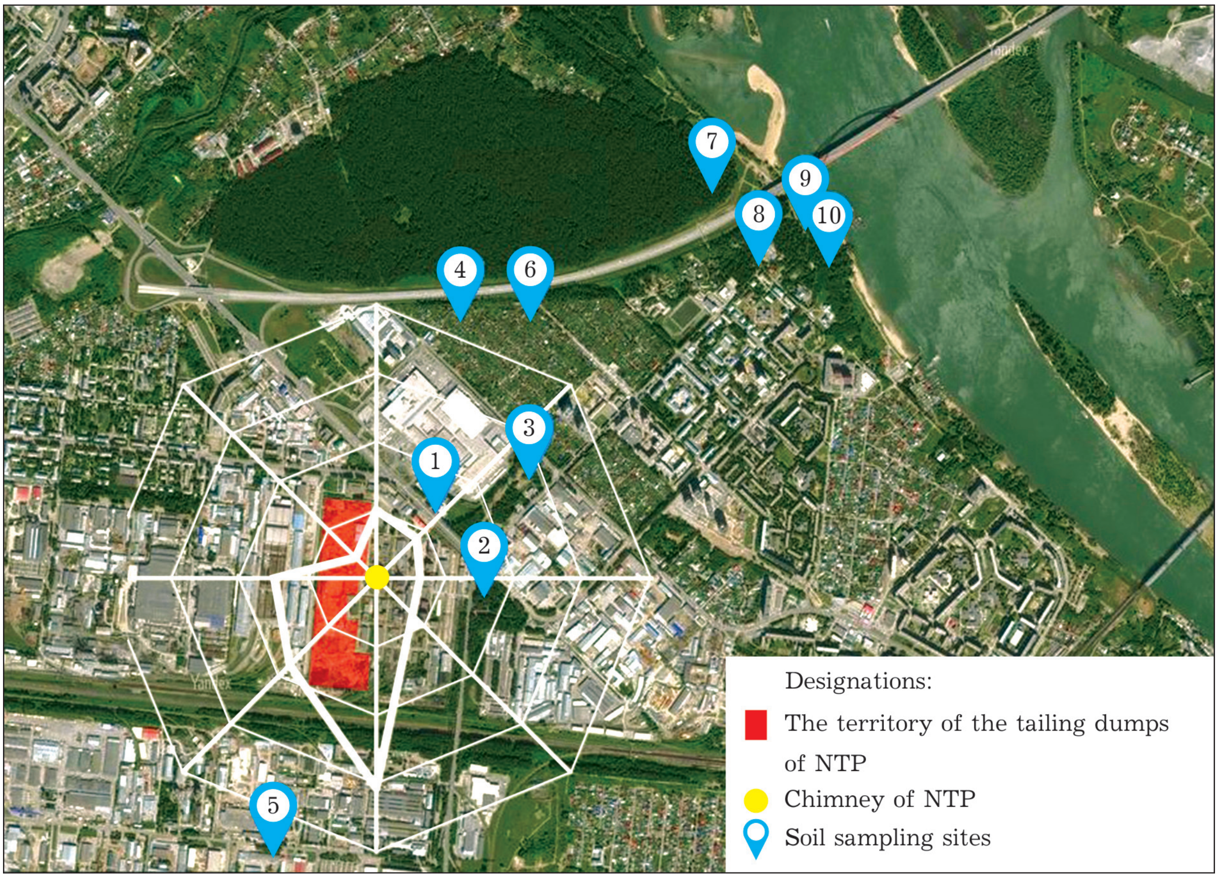

Fig. 1. Schematic map of the sampling sites with respect to the Novosibirsk Tin Plant (NTP) with the indication of wind direction frequencies for the years 1966–2018.

in area using the envelope method from the depth of 0–20 cm at a distance of 0.5–2.4 km with respect to NTP. The samples were then dried to the air-dry state at the temperature and humidity of the laboratory room, ground with a pestle in a mortar till a homogeneous state was achieved, and sieved through a kapron sieve (1 mm).

To determine the background concentrations of metals, soil samples were collected in the mouth of the Eltsovka river (the Ordynskoe district, Novosibirsk Region, coordinates: 54.443188°N, 82.308552°E). This point often serves for collecting the reference samples of soil, water and air unaffected by technogenic influence because it is at a substantial distance from industrial and agricultural enterprises [21, 22].

Analytical methods

Chemical analysis of the samples was carried out at the Laboratory of Intercalation and mechanochemical Reactions of the Institute of Solid State Chemistry and Mechanochemistry SB RAS (ISSCM SB RAS, Novosibirsk).

The content of the mobile forms of HM was determined by means of mass spectrometry with inductively coupled argon plasma (ICP-MS) with the help of an Agilent 7500a mass spectrometer (Agilent Technologies, Japan) and by means of atomic absorption using an AA-280 FS spectrometer (Varian, Australia) according to the procedure PND F 16.2.2:2.3.71-2011 “Quantitative chemical analysis of soils”. The instruments are intended for the analyses of liquid samples, so the solid samples were transferred into solution. The mobile forms of elements were extracted from the samples under analysis with the solution of nitric acid (1 mol/dm^3). Three parallel measurements were carried out for each experimental point; element content in the samples was calculated from the average value.

Some soil characteristics affecting the mobility of HM were also measured during the investigation. These characteristics include the content of organic matter, acidity, and the water regime of soil. The percentage of the organic matter was determined by annealing the weighted portions of soil in a muffle furnace according to GOST 27784-88, pH of the soil was measured using the electrometric method according to GOST 26423-85, the humidity of the soil was determined by drying the samples in the drying box to the constant mass according to GOST 5180-2015.

The level of soil pollution was established by comparing the obtained concentrations of HM in the mobile form with the maximum permissible concentrations (MPC) according to hygienic standards GN 2.1.7.2041-06. It should be noted that the MPC for arsenic is not adopted, though this is one of the most toxic elements. The authors of [23] discuss the data obtained in the studies carried out by ecologists in the Netherlands [24], according to which the content of the mobile forms of HM in the soil is standardized relying on the maximum permissible excess (MPE). This parameter is adopted for a broad range of HM (17 elements). Comparison of MPE values for some HM (Cr, Ni, Zn, Cu), for which the MPC levels have been adopted in Russia, shows that MPC and MPE values are close to each other. This allows using MPE values to evaluate the level of soil pollution with the elements for which MPC values are not adopted. So, the obtained HM concentrations will be compared for elements Cu, Pb, Ni, Cr, Zn with MPC values, which are equal to 3, 6, 4, 6, 23 mg/kg, respectively, while for As – with MPE, which is equal to 4.5 mg/kg.

To provide the ecological evaluation of soil state, we calculated concentration coefficients (K_c) for chemical substances and the total pollution index (Z_c).

The concentration coefficient K_c of a substance is defined as the ratio of the actual concentration of an element (C_i) in the sample under consideration to the background concentration of this element (C_{bi}):

$K_c = C_i/C_{bi}$

The total index of soil pollution Z_c is calculated using the equation

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

where K_{ci} is the concentration coefficient of the i^{th} component of pollution; n is the number of pollutants taken into account.

According to the methodical guide MU 2.1.7.730-99 “Hygienic evaluation of the quality of soil in residential areas”, four categories of the danger of chemical pollution of soil are distinguished with respect to the total pollution index Z_c: admissible ($Z_c < 16$), moderately dangerous ($16 < Z_c < 32$), dangerous ($32 < Z_c < 128$), extremely dangerous ($Z_c > 128$).

Mathematical statistical processing of the data was carried out using the Microsoft Excel software and included the calculation of arithmetic mean, standard deviation and other statistical parameters.

RESULTS AND DISCUSSION

The soils under analysis are characterized by the neutral, weakly alkaline and alkaline reaction, the acidity parameter (pH) varies within the range 6.9–8.5. In neutral soils (pH 6.6–7.0), the compounds of As and Zn are mobile. With an increase in pH, anion-forming elements (Cr, V, Mo, *etc.*) become mobile. In acid soils, the mobility of cation-forming metals (Zn, Cu, Pb, *etc.*) increases [11].

Accumulation of the mobile forms of elements depends on the water regime of soil, which is characterized by moisture content. The moisture content of the samples under investigation varies within the range 6–23 %, therefore, a nonpercolative regime is characteristic of soil. HM are accumulated more actively with this regime than in the soil with the percolative regime, so the fraction of potentially mobile HM increases [12].

The solid phase of soil is composed of organic and mineral parts. The high content of the organic matter in the soil allows the formation of complex compounds with HM, which is less available for plants. The percentage of the organic matter in the soil under investigation is within the range of 10–29 %. This means that the danger of the accumulation of an excessive amount of the mobile forms of elements in plants is higher than in soils with a high content of organic matter.

The entire set of the facts listed above allows us to conclude that there are prerequisites for the accumulation of HM in the soil in the industrial zone of Novosibirsk under investigation.

The plants absorb only the mobile part of HM, so it is important for the evaluation of toxicity to know the content of the elements in mobile forms. The concentrations of the mobile forms of HM in soil samples under investigation and the standards are presented in Fig. 2. A comparative analysis of the results of the investigation with the permissible HM concentrations demonstrated that the MPC are exceeded for Cu, Ni, Cr, Pb, Zn and MPE As. Therefore, soil pollution in the region affected by the metallurgical plant is polyelemental by its nature.

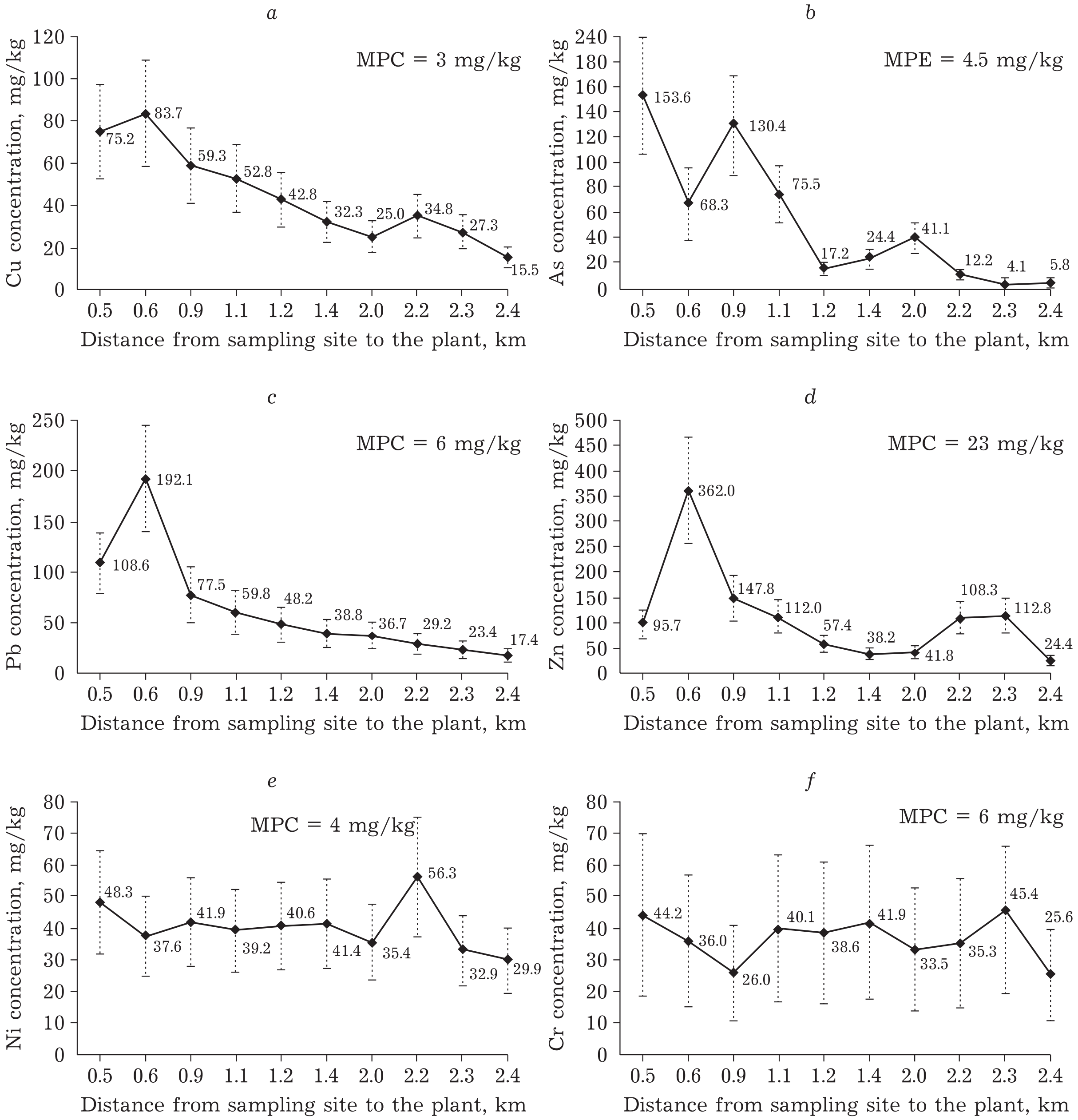

Fig. 2. Dependence of the concentrations of heavy metals on the distance from sampling sites to the Novosibirsk Tin Plant (the number of soil samples is 10, the number of parallel measurements is 3, $P = 0.95$).

The highest soil pollution with copper, zinc, lead was detected at a distance of 0.6 km from NTP. The standards for Cu, Zn, Pb were exceeded by a factor of 28, 16, 32, respectively. The maximal concentration of As (34MPE) is observed at a distance of 0.5 km, Ni (14MPC) – at a distance of 2.2 km, Cr (8MPC) – at a distance of 2.3 km. This is explained by the fact that a smaller amount of HM compounds is deposited near the plant because the scattering of the pollutants depends on the height of emission sources.

To determine the dependence of HM concentrations on the distance from sampling sites to NTP, 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 NTP contaminates the adjacent territory with copper, arsenic, lead and zinc. With an increase in the distance from the plant, their concentrations decrease. Soil pollution with nickel and chromium may be due to the effect of other technogenic sources. An answer to this question requires a de-

TABLE 1

Background concentrations of the mobile forms of heavy metals in soil samples for Novosibirsk (with 5 reference samples, three parallel measurements, $P = 0.95$)

The class of danger	Element	Concentration, mg/kg
1	As	0.98±0.49
	Pb	3.15±1.13
	Zn	8.67±3.81
2	Ni	5.20±2.18
	Cu	2.05±0.86
	Cr	4.75±2.76

TABLE 2

Concentration coefficients for the mobile forms of heavy metals (number of samples: 10, $P = 0.95$)

Element	Concentration coefficient, K_c
As	54.3±2.7
Cu	21.9±1.1
Pb	20.1±1.0
Zn	12.7±0.6
Ni	7.8±0.4
Cr	7.7±0.4

tailed investigation of the technological processes of other plants situated in this industrial zone.

Results of the determination of background concentrations (C_{bi}) of HM in soil samples for Novosibirsk are shown in Table 1. One can see that these concentrations except Ni do not exceed the MPC level.

Concentration coefficients (K_c) calculated for each element from the experimentally obtained data are presented in Table 2. According to this parameter, the sequence of the accumulation of mobile HM forms in the soil of the industrial zone near NTP is Cr < Ni < Zn < Pb < Cu < As.

The total pollution index (Z_c) for the territory under consideration is equal to 125, which corresponds to the dangerous extent of soil pollution ($32 < Z_c < 128$). According to the methodical guide MU 2.1.7.730-99 this level of pollution is characterized by a possible increase in total morbidity of the population in the vicinity of the plant, and an increase in the number of persons with chronic diseases.

CONCLUSION

Pollution of the soil in the industrial zone of Novosibirsk in the region affected by NTP is polyelemental by its nature. Within the territory under study, the concentrations of the mobile forms of Cr, Ni, Pb, Cu, Zn exceed the MPC over the whole territory, and As content does not exceed MPE only at a distance of 2.3 km from the tin plant.

The total index of soil pollution with HM shows that according to the established sanitary standards of the RF, these soils are characterized by a dangerous degree of chemical pollution.

The highest danger is in the pollution of soils of garden plots in the Kirovskiy region with the mobile forms of HM because there is the risk of HM migration along food chains into human organisms. The content of arsenic, which is recognized as the 1st group carcinogen, reaches 34MPE; the excess for Ni and Pb (carcinogens of group 2) is 14MPC and 32MPC, respectively.

The pollution with HM revealed in the industrial zone provides evidence of the necessity of remediation (purification) of contaminated soil.

The authors express sincere gratitude to researchers from the Institute of Solid State Chemistry and Mechanochemistry SB RAS A. L. Bychkov, I. A. Derevyagina and N. F. Glazyrina for assistance in carrying out this research.

REFERENCES

1 Barsova N., Yakimenko O., Tolpeshta I., Motuzova G., Current state and dynamics of heavy metal soil pollution in Russian Federation – A review, *Environmental Pollution*, 2019, Vol. 249, P. 200–207.

2 Emelyanova N., Naprasnikova E., Sorokovoi A., The ecological state of a large city of Eastern Siberia in the process of urbanization, *Geography and Natural Resources*, 2018, Vol. 39, No. 4, P. 324–331.

3 Minkina T., Sushkova S., Konstantinov A., Rajput V., Sherstnev A., Urban soil geochemistry of an intensively developing Siberian city: A case study of Tyumen, Russia, *Journal of Environmental Management*, 2019, Vol. 239, P. 366–375.

4 Kosheleva N. E., Vlasov D. V., Korlyakov I. D., Kasimov N. S., Contamination of urban soils with heavy metals in Moscow as affected by building development, *Science of the Total Environment*, 2018, Vol. 636, P. 854–863.

5 Singh N., Gupta V., Kumar A., Sharma B., Synergistic effects of heavy metals and pesticides in living systems, *Frontiers in Chemistry*, 2017, Vol. 5, Article 70. DOI: 10.3389/fchem.2017.00070

6 Wang P., Sun Z., Hu Y., Cheng Y., Leaching of heavy metals from abandoned mine tailings brought by precipitation and the associated environmental impact, *Science of the Total Environment*, 2019, Vol. 695, Article 13893. https://doi.org/10.1016/j.scitotenv.2019.133893

7 Jaishankar M., Tseten T., Anbalagan N, Mathew B. B., Toxicity, mechanism and health effects of some heavy metals, *Interdisciplinary Toxicology*, 2014, Vol. 7, No. 2, P. 60–72.

8 Al-Saleh I., Al-Rouqi R., Elkhatib R., Abduljabbar M., Al-Rajudi T., Risk assessment of environmental exposure to heavy metals in mothers and their respective infants,

International Journal of Hygiene and Environmental Health, 2017, Vol. 220, P. 1252–1278.

9 Jarup L., Hazards of heavy metal contamination, *British Medical Bulletin*, 2003, Vol. 68, P. 167–82.

10 Shcherbakova I. N., Gustaitis M. A., Lazareva E. V., Bogush A. A., Migration of heavy metals (Cu, Pb, Zn, Fe, Cd) in the aureole of scattering at the Urskoye tailing dump (Kemerovo Region), *Chemistry for Sustainable Development*, 2010, Vol. 18, No. 5, P. 535–547.

11 Gaskova O. L., Bortnikova S. B., Kabannik V. G., Novikova S. P., Features of soil pollution in the region of storage of the wastes from pyrometallurgical zinc extraction at the Belovo Zibc Plant, *Chemistry for Sustainable Development*, 2012, Vol. 20, No. 4, P. 375–384.

12 Ettler V., Soil contamination near non-ferrous metal smelters: A review, *Applied Geochemistry*, 2016, Vol. 64, P. 56–74.

13 Vlasov O. A., Processes of Obtaining Metals [notes of lectures] [in Russian], Krasnoyarsk: SFU ITsMiM. URL: https://studfile.net/preview/7225806/ (Accessed 07.12.2019).

14 Raputa B. F., Shuvaeva O. V., Kokovkin V. V., Shurukhin S. G., Vorobyeva O. A., Analysis of aerosol pollution near the Novosibirsk Tin Plant, *Chemistry for Sustainable Development*, 2002, Vol. 10, No. 5, P. 641–647.

15 Kokovkin V. V., Raputa V. F., Shuvaeva O. V., Monitoring of the heavy metal pollution of snow cover in the vicinity of the Novosibirsk Tin Plant [in Russian], *Interekspo GEO-Sibir*, 2013, Vol. 4, No. 2, P. 36–41.

16 Artamonova S. Yu., Raputa V. F., Kolmogorov Yu. P., Technogenic pollution of soil and vegetation cover near the tin plant (Novosibirsk) [in Russian], *Interekspo GEO-Sibir*, 2005, Vol. 5, P. 106–110.

17 Baran A., Tarnawski M., Assessment of heavy metals mobility and toxicity in contaminated sediments by sequential extraction and a battery of bioassays, *Ecotoxicology*, 2015, Vol. 24, No. 6, P. 1279–1293.

18 Prabhat K., Sang S., Ming Z., Yiu F., Heavy metals in food crops: Health risks, fate, mechanisms, and management, *Environment International*, 2019, Vol. 125, P. 365–385.

19 Regulation No. 1091 of 27.03.2018 "The project of planning and the projects of land marking of the territory restricted by Vatutin street, Sovetskoe road, Petukhov street, Sibiryakov-Gvardeytsev street, the Tula river, in the Kirovskiy region (with changes introduced on June 4, 2018)". The Novosibirsk Mayor's Office. URL: http://docs.cntd.ru/document/465721241 (Accessed 01.10.2018). (in Russ.).

20 West Siberian Department of Gydrometeorology and Environmental Protection. Official observation data. Official forecasts. The wind rose per year. URL: http://www.meteonso.ru/pages/53 (Accessed 11.09.2018). (in Russ.).

21 Skripkina T. S., Bychkov A. L., Smolyakov B. S., Changes in phytoplankton production after the introduction of heavy metals into ecosystem with subsequent cleaning by humic sorbent, *Water Resources*, 2019, Vol. 46, No. 2, P. 242–248.

22 Skripkina T., Bychkov A., Tikhova V., Smolyakov B., Lomovsky O., Mechanochemically oxidized brown coal and the effect of its application in polluted water, *Environmental Technology and Innovation*, 2018, Vol. 11, P. 74–82.

23 Vodyanitskiy Yu. N., Norms of the content of heavy metals and metalloids in soil [in Russian], *Pochvovedenoye*, 2012, No. 3, P. 368–375.

24 Crommentuijn T., Polder M. D., Van de Plassche E. J.Б Maximum Permissible Concentrations and Negligible Concentrations for Metals, Taking Background Concentrations into Account, RIVM Rapport 601501001, Bilthoven, Netherlands, 1997. 260 p. URL: https://www.rivm.nl/bibliotheek/rapporten/601501001.pdf (Accessed 24.02.2020).