POLISH JOURNAL OF NATURAL SCIENCES
Abbrev.: Pol. J. Natur. Sc., Vol 34(2): 245–256, Y. 2019

HEAVY METALS POLLUTION OF SMALL URBAN LAKES SEDIMENTS WITHIN THE ONEGO LAKE CATCHMENT AREA*

***Aleksandr Medvedev*[1], *Zakhar Slukovskii*[2], *Dmitry Novitcky*[3]**

[1] ORCID: 0000-0001-8234-156X
[2] ORCID: 0000-0003-2341-361X
[3] ORCID: 0000-0003-0342-0249
Institute of Geology
Karelian Research Center, Russian Academy of Sciences in Petrozavodsk, Russia

Key words: sediments, heavy metals, geo-accumulation index, pollution.

Abstract

A geochemical investigation of two sediment cores retrieved from Plotich'e and Kitaiskoe lakes (Republic of Karelia, Russia) has been carried out. The content of eight heavy metals (Pb, Cd, Zn, Cr, Ni, Cu, Mn, and V) in the modern bottom sediments was determined. The sources of pollution of the sediments of the lake have been revealed. In order to estimate the negative impact of human activities on the urban lakes, the geo-accumulation index has been calculated. It is noted that Plotich'e and Kitaiskoe lakes are contaminated by heavy metals in different ways.

Introduction

Waterbodies, which are located either within urban areas or nearby towns, are permanently subjected to anthropogenic load. The extent of the load can be determined via the investigation of the chemical composition of both water and sediments. Lakes, as a rule, are considered as a landscape depression, since they are capable of the accumulation of natural material (DAUVALTER et al. 2011), delivered from the catchment area through rivers as well as temporary flows. As a result, lacustrine sediments (especially closed-basin lakes sediments) are considered as perfect archi-

Address: Aleksandr Medvedev, Karelian Research Center, Russian Academy of Sciences in Petrozavodsk, Pushkinskaya 11, 185910, Petrozavodsk, Republic of Karelia, Russia, phone: +7 (8142) 76 60 40, e-mail: sanjam22@mail.ru

* The reported study was funded by according to the RFBR research project No 18-05-00897 and the grant of the President of the Russian Federation No. MK-462.2019.5.

ves (Sun et al. 2009). These can be used for reconstructing past sedimentation processes, assessment of the modern ecological conditions, and prognostication of possible ways of changing in the future.

The purposes of this survey are to define the heavy metals content in the lake sediment cores, which were retrieved from the central parts of Plotich'e and Kitaiskoe lakes (Medvezhyegorsk town, Republic of Karelia) and to the main sources of heavy metals input to these waterbodies.

Research area, Materials and Methods

Medvezhyegorsk is a small town with population of 15 thousand people, which is situated in the central part of Karelia Republic. The town is washed by Poveneckii bay (Onego lake) from the south. The main possible sources of urban environment pollution are railway and automobile mean of transport, a crushed stone quarry, a milk plant, a bakery plant and a number of woodworking enterprises.

Plotich'e lake (Figure1) is a small water body, which is situated in the West part of Medvezhyegorsk. This water object is actively used in household and recreation purposes (swimming, fishing). In March of 2016, a 28-cm sediment core was retrieved from the central part of the lake (the site's depth is roughly 20 m) through a Limnos sampler. The total number of samples obtained from this lake was 13. The sediment core, except the bottom 4 cm, was split into 2 cm layers and sealed in plastic containers.

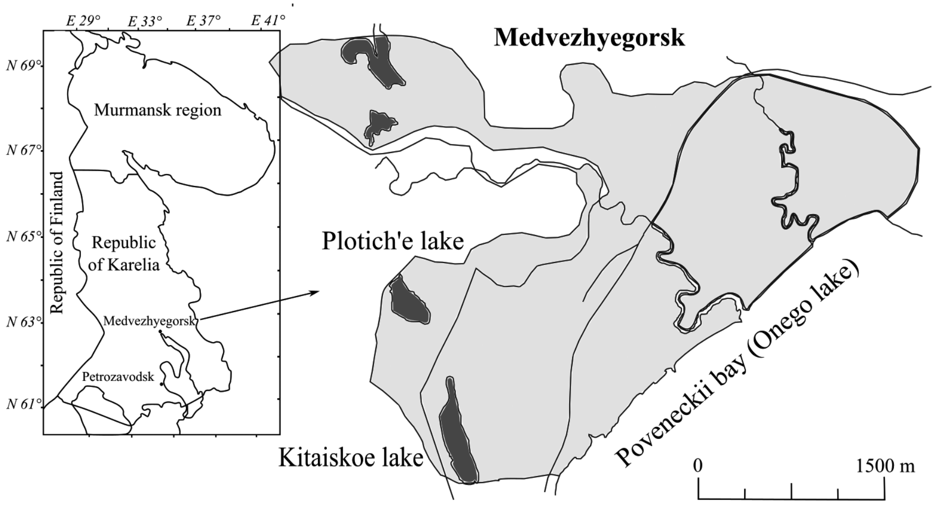

Fig 1. Map of the research area

Kitaiskoe lake (Figure 1) is also a small water body, which is located in the South-West part of the town. This lake is mostly used by domestic fishermen. In June of 2016, a 20-cm sediment core was retrieved from the central part of the lake (depth is approximately 26 m) through a Limnos sampler. The total number of samples obtained from this lake was 10. The sediment core was split into 2 cm layers and sealed in plastic containers.

Each 2 cm layer was put into a refrigerator bag and transported to the Institute of Geology RAS, Petrozavodsk. Dried sediment samples were then decomposed by acid autopsy with an acid mixture in an open system. The method for preparing the samples for chemical analysis was described in (SLUKOVSKII and POLYAKOVA 2016). Metal concentrations in the bottom sediment samples were estimated using the mass-spectral method on a XSeries-2 ICP-MS instrument at the Analytical Centre of the Institute of Geology, KarRC, RAS, Petrozavodsk. Each sample was measured in three repetitions. The final concentration is an average of these repetitions. The geo-accumulation index I_{geo} of heavy metals in bottom sediments was calculated using the formula:

$$I_{\mathrm{geo}} = \log_2\left(\frac{C}{1.5B}\right),$$

where C is the metal concentration in the layer of interest, B is background metal concentration measured in the deepest layer of the core (GUPTA et al. 2014). The concentrations of heavy metals in the lowest layers were accepted as the background for each of the researched lakes.

Results and Discussion

Table 1 and Table 2 represent information about the concentration of eight heavy metals in sediments of Plotiche and Kitaiskoe lake. As it can be seen from the data, the ***lead*** concentration reaches its peak (155 mg kg^{-1}) in the 6–8 cm layer of sediment core retrieved from Plotiche lake, while the maximal rate of the element (42.6 mg kg^{-1}) in Kitaiskoe sediment core was detected in the 4–6 cm layer. In general, both lakes have similar lead content through sediments columns. The largest values were ascertained in the upper 14 cm layers. Then there is a noticeable decrease in the lead concentration in the underlying layers. The average concentration of the element in sediments accounts for 62.7 mg kg^{-1} for the former lake and 26.4 mg kg^{-1} for the latter.

Table 1

Concentration of heavy metals in Plotiche lake sediments [mg kg^{-1}]

Specification	Pb	Cd	Zn	Cr	Ni	Cu	Mn	V
0–2	79.4	1.24	577	41.7	40.8	**790**	363	101
2–4	89.6	1.53	563	42.8	41.5	105	306	96.6
4–6	113	1.81	**624**	53.6	45.4	70.5	330	106
6–8	**155**	**2.03**	571	60.2	45.4	90.9	353	95.4
8–10	104	1.62	339	60.7	43.6	61.9	**371**	78.9
10–12	77.8	1.28	191	45.3	34.6	47.0	338	76.4
12–14	55.7	1.38	123	**73.1**	**60.6**	54.7	301	103
14–16	32.6	0.80	113	23.5	24.3	21.3	228	121
16–18	30.7	0.58	123	25.8	25.7	23.6	240	128
18–20	24.0	0.46	67.7	19.3	21.1	16.9	205	109
20–22	26.2	0.52	70.5	20.8	22.6	18.9	215	109
22–24	24.6	0.46	63.2	20.1	21.9	17.1	213	109
24–28	2.60	0.34	97.6	21.3	18.1	19.8	164	**160**
X Average	62.7	1.08	271	39.1	34.3	103	279	107

Table 2

Concentration of heavy metals in Kitaiskoe lake sediments [mg kg^{-1}]

Specification	Pb	Cd	Zn	Cr	Ni	Cu	Mn	V
0–2	35.4	1.24	**391**	19.9	30.3	**47.6**	**1713**	26.2
2–4	39.8	1.27	384	19.8	27.6	44.5	1578	26.7
4–6	**42.6**	1.28	380	20.9	**31.0**	47.1	1600	**27.2**
6–8	42.4	**1.31**	361	20.1	30.1	45.4	1453	24.8
8–10	38.6	0.85	283	19.4	29.2	42.1	1127	23.2
10–12	27.0	0.73	228	18.4	27.1	33.9	1178	19.2
12–14	23.3	0.71	215	**21.5**	26.2	38.9	1041	18.5
14–16	7.06	0.24	82.0	18.6	24.8	37.3	690	16.4
16–18	2.74	0.17	45.2	16.9	24.1	31.5	550	15.6
18–20	5.36	0.25	85.3	17.9	25.0	53.7	428	21.9
X Average	26.4	0.81	245	19.3	27.5	42.2	1136	22.0

According to the tables, the **cadmium** concentration has its maximal rate in the 6–8 cm layer in both lakes. It amounts to 2.03 mg kg^{-1} in Plotiche and 1.31 mg kg^{-1} in Kitaiskoe lakes sediments. As in the case with lead distribution, the highest concentrations of cadmium were detected in the upper 14 cm layers of both sediment cores, while the rates of the heavy metal in the underlying layers do not exceed the average concentrations for both columns.

The upper 10 cm of a Plotich'e lake sediment core is considerably contaminated with **zinc**. The 4–6 cm layer has the maximal rate of the element – 624 mg kg^{-1}. The minimal concentration – 63.2 mg kg^{-1} was detected in the 22–24 cm layer. The highest rates of zinc in Kitaiskoe lake sediments core has been concentrated in the first 14 cm layers with a maximum of 391 mg kg^{-1} in the 0–2 cm layer. The lower concentration of the element was ascertained in the 16–18 cm layer.

The maximal concentration of **chromium** – 73.1 mg kg^{-1} in sediments of Plotich'e lake was detected in the 12–14 cm layer. The minimal rate of the element – 19.3 mg kg^{-1} is concluded in the 18–20 cm layer. In general, the chromium average rate of the upper 14 cm of the column is roughly twice higher than the bottom 14 cm one. In contrast, the content of chromium in Kitaiskoe lake sediments varies inconsiderably throughout the column. The maximal rate of the element – 21.5 mg kg^{-1} was detected in the 12–14 cm layer, while the minimal chromium concentration – 16.9 mg kg^{-1} was found in 16–18 cm layer.

As in the case with chromium distribution in the Plotich'e lake sediment core, the maximal rate of **nickel** – 60.6 mg kg^{-1} was found in the 12–14 cm layer of the column retrieved from the lake. The minimal concentration of the heavy metal –18.1 mg kg^{-1} was detected in the bottom 4-cm layer. The maximal value of nickel in Kitaiskoe lake sediment core – 31.0 mg kg^{-1} was detected in the 4–6 cm layer, while the minimal content of the element – 24.1 mg kg^{-1} was found in the 16–18 cm layer.

The concentration of **copper** ranging from a maximum of 790 mg kg^{-1} in the first 2-cm layer to a minimum of 16.9 mg kg^{-1} in the 18–20 cm layer in Plotiche lake sediments and from the largest of 47.6 mg kg^{-1} in the first 2-cm layer to a low of 31.5 mg kg^{-1} in the 16–18 cm layer in Kitaiskoe lake sediments.

The highest concentrations of **manganese** were established in the uper sediment 14-cm layers of both lakes. However, there is a substantial difference in the values of the heavy metal in these two lakes. The content of manganese for Plotiche lake ranging from a maximum of 371 mg kg^{-1} in the 8–10 cm layer to minimum of 164 mg kg^{-1} in the 24–28 cm layer, while sediment core retrieved from Kitaiskoe lake has the maximal rate of the element equals to 1713 mg kg^{-1} (found in the 0–2 cm layer) and minimal rate equals to 428 mg kg^{-1} (found in the 18–20 cm layer).

The concentration of **vanadium** in sediments of both lakes varies inconsiderably throughout the columns. In Plotiche lake sediments the highest concentration of the element – 160 mg kg^{-1} was found in the bottom 4-cm layer. In sediments of Kitaiskoe lake, on the contrary, the maximal rate of vanadium was detected in 4–6 cm layer.

In order to estimate the extent of anthropogenic influence on the heavy metals concentrations in the sediments of these waterbodies, the geoaccumulation index was used. The index is calculated through the formula: $I_{geo} = \log_2 (C/1.5B)$, where C is the measured concentration of the element in the sediments fraction, B is the geochemical background value, 1.5 is the correction factor due to lithological variations (MÜLLER 1979). According to FORSTNER et al. (1993), the geoaccumulation index classification consists of 7 grades (Table 3).

Table 3

Index of geoaccumulation and contamination levels

Sediment Igeo contamination value	Geoaccumulation class Intensity	Index, Igeo (sediment quality)
>5	6	very strong
>4–5	5	strong to very strong
>3–4	4	strong
>2–3	3	moderate to strong
>1–2	2	moderate
>0–1	1	uncontaminated to moderate
>0	0	practically uncontaminated

Source: GUPTA et al. (2014)

As it can be seen from the Figure 2, the first 2-cm layer of Plotich'e lake sediment core has a very strong Cu contamination (class 6), strong to very strong Pb contamination (class 5), and moderate to strong Zn contamination (class 3). The 2–6 cm layer is polluted by Pb (class 5), Cu (class 3), and Zn (class 3). The 6–8 cm layer is also contaminated by Pb (class 5), Cu and Zn (class 3) plus there appeared Cr contamination (class 3). The 8–10 cm layer is polluted by Pb (class 5) and Cr (class 3). In the 10–12 cm layer just Pb contamination (class 4) was found. The 12–14 layer is contaminated by Pb (class 4), Cr (class 3), and Ni (class 3). The 14–24 cm layer is only contaminated by Pb, values for this heavy metal are in class 3. The bottom 4 cm layer of the sediment core does not consist of any heavy metals contamination footprints.

The upper 8 cm layer of Kitaiskoe lake sediment core is characterized by high values for Mn (class 4), Pb (first 2 cm layer – class 3, 4–8 cm layer – class 4), and Zn (class 3) – Figure 3. The 8–14 cm layer is strongly polluted by Mn (class 4) and has moderate to strong Pb pollution (class 3). In the 14–18 cm layer moderate to strong Mn contamination was detected. The bottom 2 cm layer has no heavy metal pollution.

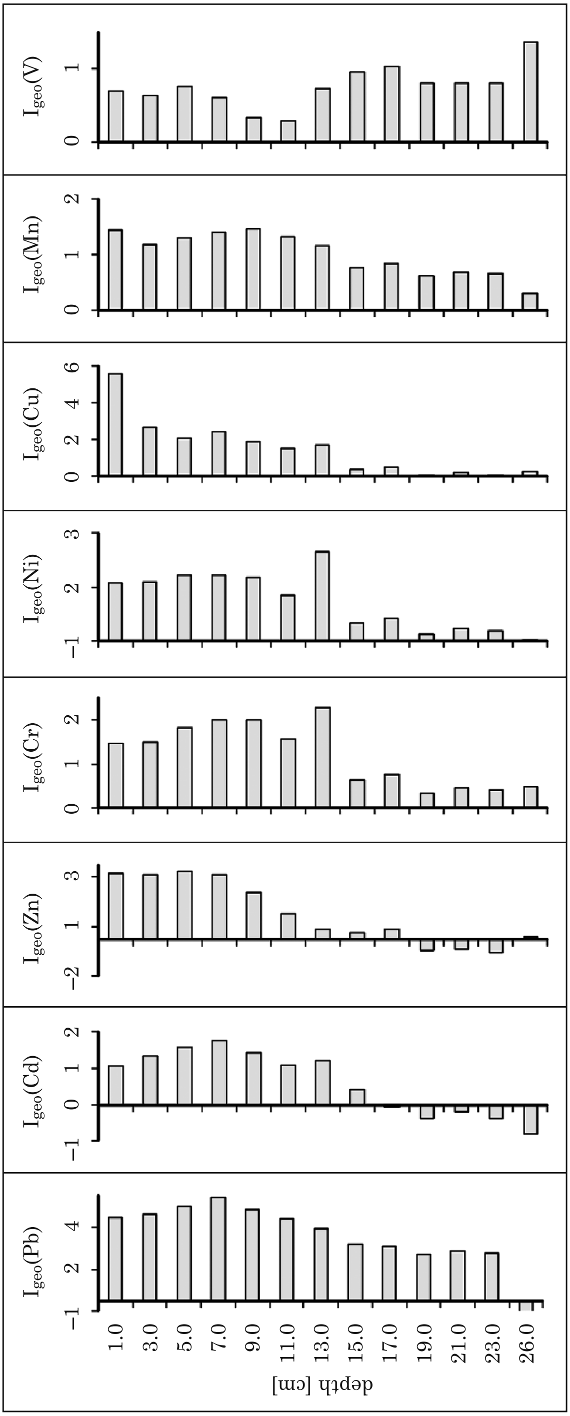

Fig. 2. Values of the geo-accumulation index (I_{geo}) of heavy metals in Plotich'e lake sediments

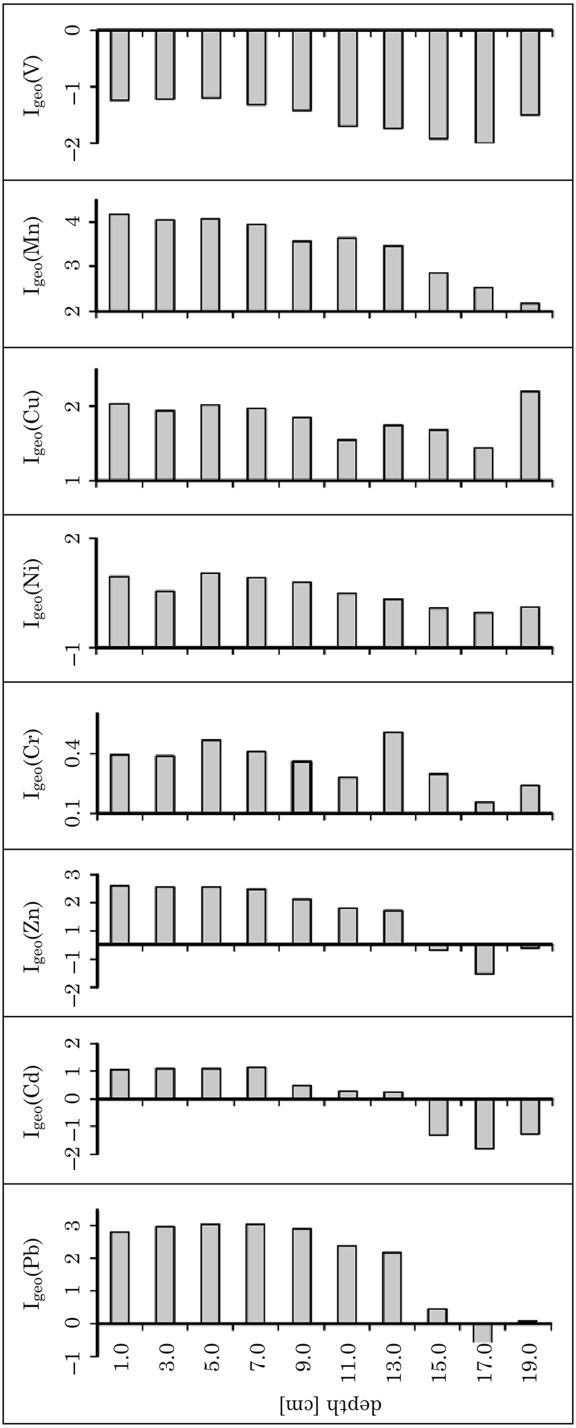

Fig. 3. Values of the geo-accumulation index (I_{geo}) of heavy metals in Kitaiskoe lake sediments

According to the calculations, copper has the maximal value of geoaccumulation index (5.6) among the eight heavy metals and it is observed only in the upper 2 cm layer of the sediment core retrieved from Plotich'e lake. Kitaiskoe lake, on the contrary, doesn't have high levels of the element throughout the whole sediment column. It could be connected with the fact that copper is used in agriculture (fertilizer and pesticides) (KABATA-PENDIAS and MUKHERJEE 2007). Because Plotich'e lake is located in a zone of housing with a plethora of private kitchen-gardens, which are located up to the territory of the lake, it is possible that this heavy metal is delivered into the waterbody through the surface flows. Seemingly, copper precipitates and gets "fixed" in the surficial sediment layer of the lake, which could be considered as a vertical geochemical barrier between the water and sediments. Kitaiskoe lake, by contrast, is rather secluded from any dwelling and agricultural objects. So, the Cu content in the sediments of the lake is considerably lower, than in the Plotich'e lake sediments.

Lead also has a rather high value of the geoaccumulation index, especially in the upper 10 cm layer of sediment core sampled from Plotich'e lake, reaching its peak at 4.9 in the 6–8 cm layer. The maximal value of the geoaccumulation index for Pb in Kitaiskoe lake sediments (3.1) was found in the 4–8 cm layer. Exceeded lead content in the sediments is probably connected with the effect of global pollution by Pb compounds (MCCONNEL and EDWARDS 2008, NORTON et al. 1990), such as tetraethyl lead, which was actively used in knock-sedative dope in gasoline in the middle of the XX century (NRIAGU 1990, KOMAREK et al. 2008). This metal together with Cd and Sb from the lake sediments of the Republic of Karelia, the Murmansk Region and Finland, including Arctic zone of these territories, behave in a similar manner (UKONMAANAHO et al. 1998, VERTA and TOLONEN 1998, DAUVALTER and KASHULIN 2010, DAUVALTER et al. 2011, SLUKOVSKII et al. 2018). The influence of the long-distance air transport of heavy metals is observed in these cases (VINOGRADOVA et al. 2017).

Moderate to strong zinc pollution is revealed in the upper 8 cm sediments layer of both lakes. Zinc contamination could be related to non-ferric metal industry (KABATA-PENDIAS and MUKHERJEE 2007). Possibly, the high level of this metal in the sediments caused by the activity of the Nadvoickii aluminum plant, which is located 100 km northward from Medvezhyegorsk town. The plant was placed in operation in 1954, for this reason, Zn contamination is observed only in the first 8 cm of both sediment cores.

Manganese contamination from strong to moderate is observed through the whole sediment core of Kitaiskoe lake, except of the bottom 2 cm. Sediments from Plotich'e lake, by contrast, do not have any traces of high

Mn concentration. Inasmuch as the manganese content could be connected with igneous rocks and glacial depositions (MARTYNOVA 2012), it is possible that it has entered into the lake owning to intensive weathering, occurring within the local catchment area of Kitaiskoe lake.

Moderate to strong chromium pollution was found in 6–10 cm and 12–14 cm layers of Plotich'e lake sediments. Cr is used in woodworking industry as preservatives (KABATA-PENDIAS and MUKHERJEE 2007, BESSONOVA and IVANCHENKO 2011), so the chromium contamination in Plotich'e lake sediments may be caused by the activity of woodworking enterprises, which are located in Medvezhyegorsk town.

critical values

U_{Cr}	
$p \leq 0.01$	$p \leq 0.05$
27	37

level of significance

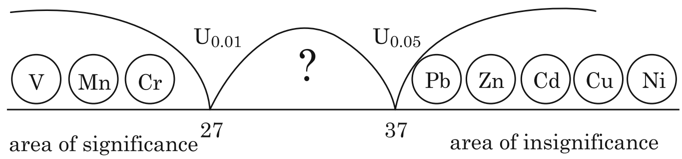

Fig 4. The Mann-Whitney U-test for heavy metals content in sediments of Plotich'e and Kitaiskoe lakes

In order to determine if there is a difference in the value of parameters between two columns of sediments, Mann-Whitney U-test was run. The test is meant to be used for comparing two independent samples, when the assumption of normality of equality of variance is not met (PEREIRA and LESLIE 2010). Figure 4 demonstrates that there is a discrepancy in V, Mn and Cr content in sediments of Plotich'e and Kitaiskoe lake, whereas the three heavy metals are in the zone of significance.

Conclusions

Thus, sediments of Plotich'e lake are mostly polluted by copper (the highest value of *I*geo – 5/6 found in the upper 2 cm layer), lead (the highest value of Igeo – 4.9 found in the 6–8 cm layer), zinc (the highest value of Igeo – 2.8 found in the 4–6 cm layer), and chromium (the highest value of Igeo – 2.3 found in the 12–14 cm layer). Also, it is considerable to point out that there is no manganese contamination in the sediment core retrieved from Plotich'e lake, while sediments of Kitaiskoe lake are contaminated by this heavy metal (the highest value of Igeo for Mn – 3.7 found in the first 2 cm layer). Other valuable contaminants revealed in sediments of the lake are lead (the highest value of Igeo – 3.1 found in the 4–8 cm layer) and zinc (the highest value of Igeo – 2.1 found in the upper 4 cm layer).

In general, it could be concluded that the highest values of pollutants are concentrated in the upper 8 cm layer of both sediment columns. The basic pollution sources of the lakes sediments are the railway and automobile means of transport, fertilizers, woodworking industry, and an aluminum plant.

Accepted for print 16.04.2019

References

BESSONOVA V., IVANCHENKO O. 2011. *Chromium in the environment.* Bioindication and Ecology Questions, 1: 13–29.

DAUVALTER V., KASHULIN N. 2010. *Chalcophile elements (Hg, Cd, Pb, As) in lake Umbozero, Murmansk Province.* Water Resources, 37(4): 497–512.

DAUVALTER V., KASHULIN N., SANDIMIROV S., TERENTJEV P., DENISOV D., AMUNDSEN P. 2011. *Chemical composition of lake sediments along a pollution gradient in a Subarctic watercourse.* Journal of Environmental Science and Health, Part A, 46: 1020–1033.

FORSTNER U., AHLF W., CALMANO W., *1993. Sediment quality objectives and criteria development in Germany.* Water Sci. Technol., 28: 307–316.

GUPTA S., VINOD J., MATIC N., KAPRALOVA V. SOLANKI J., 2014. *Assessment of geo-accumulation index of heavy metal and source of contamination by multivariate factor analysis.* Int. J. Hazardous Mater., 2: 18–22.

GUSEV O. N., SMIRNOVA N.M., LISKOVICH A.L., KLINTEVICH V., BOLSHAKOVA L., SOKOLOVA L. 2000. *Assessment of the status and prospects of development of the mineral resource base of peat and sapropel on the North-West of the Russian Federation.* Respublika Kareliya, SPb.

KABATA-PENDIAS A., MUKHERJEE A. 2007. *Trace elements from soil to Human.* Springer-Verlag.

KOMÁREK M., ETTLER V., CHRASTNÝ V., MIHALJEVI M. 2008. *Lead isotopes in environmental sciences:* A review Environ. Int.V. 34(4): 562–577.

MARTYNOVA M.V. 2012. *Manganese forms, their contents, and transformation in freshwater sediments (analytical review).* Ekol. Khim., 21(1): 38–52.

MCCONNELL J., EDWARDS R. 2008. *Coal burning leaves toxic heavy metal legacy in the Arctic.* Proceedings of the National Academy of Sciences, 34: 12140–12144.

NRIAGU J. 1990. *The rise and fall of leaded gasoline.* Science of the Total Environment, 92: 13–28.

NORTON S.A., DILLON P.J., EVANS R.D. 1990. *The history of atmospheric deposition of Cd, Hg and Pb in north America: Evidence from lake and peat bog sediments.* Sources, Deposition and Capony Interactions, III: 73–101.

PEREIRA S.M.C, LESLIE G. 2010. *Testing differences between two samples of continuous data.* Australian Critical Care, 23: 160–166.

SLUKOVSKII Z.I., POLYAKOVA T.N. 2017. *Analysis of accumulation of heavy metals from river bottom sediments of the urban environment in the bodies of Oligochaetes.* Inland Water Biology, 10(3): 315–322.

SLUKOVSKII Z.I., SHELEKHOVA T.S., SIROEZHKO E.V. 2018. *A response of diatoms from the small lake on heavy metals effect in an urban environment, Republic of Karelia.* Vestnik of Saint Petersburg University. Earth Sciences, 63(1): 103–123.

SUN Q., WANG S., ZHOU J., CHEN Z., SHEN J., XIE X, WU F., CHEN P. 2009. *Sediment geochemistry of Lake Daihai, north-central China: implications for catchment weathering and climate change during the Holocene.* J. Paleolimnol., 43: 75–87.

UKONMAANAHO L., STARR M., HIRVI J.P., KOKKO A., LAHERMO P., MANNIO J., PAUKOLA T., RUOHO-AIROLA T., TANSKANEN H. 1998. *Heavy metal concentrations in various aqueous and biotic media in Finnish Integrated Monitoring catchments.* Boreal Environment Research, 3: 235–249.

VERTA M., TOLONEN K. 1998. *History of heavy metal pollution in Finland as recorded by lake sediments.* The Science of Total Environment, 87/88: 1–18.

VINOGRADOVA A., KOTOVA E., TOPCHAYA V. 2017. *Atmospheric transport of heavy metals to regions of the North of the European territory of Russia.* Geography and Natural Resources, 38(1): 78–85, https://doi.org/10.1134/S1875372817010103.