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THE ENVIRONMENTAL GEOCHEMISTRY OF RECENT SEDIMENTS OF SMALL LAKES IN THE SOUTHWEST OF KARELIA, RUSSIA

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Abstract

In this article, issues of environmental pollution due to long-range atmospheric transport of heavy metals are considered. Researches of recent sediment cores of Lakes Liunkunlampi and Raivattalanlampi from the Republic of Karelia were carried out. The purpose of the study was to give a detailed environmental and geochemical assessment of the recent sediments in these small lakes located in the southwestern part of Karelia. The scope of the study covers the area of the southwest of Karelia (Russia) and touches the environmental problems of northern Europe. The maximum of heavy metal accumulation appears in the upper sediment layers from 0 to approximately 15 cm. The main pollutants of the lakes are Pb, Cd, Zn, Cu, Sb, Sn, Bi, and Tl, which are geochemistry agents of long-range pollutant transport from anthropogenic sources of Russia, Finland and other countries of Northern and Eastern Europe. It was revealed that the type of sediments significantly influences the activity of heavy metal accumulation. The sediments of Lake Liunkunlampi contain more heavy metal concentrations than sediments of Lake Raivattalanlampi, because Liunkunlampi sediments consist of about 80% organic matter, whereas Raivattalanlampi sediments are made up of 26% organic matter. Analysis of fractions of heavy metals illustrated that pollutants basically are bound with mineral and organic phases of lake sediments in south-west Karelia. The high bioavailable of some metals (Cd, Pb, Zn) are noted.

Keywords: lake sediments, fractions of pollutants, heavy metals, Republic of Karelia, sapropel, small lakes

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1. Introduction

The bottom sediments of lakes (hereinafter referred to as 'sediments') is an indicator of various processes occurring in water bodies and their respective catchment areas (Förstner et al., 2004). Paleolimnological reconstructions based on detailed studies of stratified core samples of sediments have been undertaken in all of the world's regions, including the northern hemisphere, where multiple lakes and other water bodies are found (Dauvalter et al., 2011; Moiseenko et al., 2000; Rognerud and Fjeld, 2001; Subetto et al., 2017; Verta et al., 1998). The Republic of Karelia (Russia) is one such region. Nearly 61,000 lakes are registered in Karelia, most of them classified as small lakes with a surface area of not more than 1 km^2 (Filatov and Kukharev, 2013; Sinkevich and Ekman, 1995).

The most common sediment type in such lakes is sapropel, which is rich in organic matter (Strakhovenko et al., 2014). However, the top layer of sediments may contain a significant share of pollutants, including heavy metals originating from both local sources of pollution and industrial sites located a considerable distance from the water body (Bartnicki, 1994). Paleolimnological reconstruction can not only reveal the recent (over the past five to ten years) level of anthropogenic impacts on the

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ecosystem but also makes it possible to reliably identify the sequence of anthropogenic events in the study area from the beginning of the industrial era (Dauvalter and Kashulin, 2010; Kuwae et al., 2013).

According to numerous studies, metals such as Pb, Cd, Tl, Sb, Sn, Zn, Cu and Bi are geochemical markers of the anthropogenic transformation of the natural environment in areas removed from direct anthropogenic impact (Feng et al., 2016; Johansson et al., 2001; Kuwae et al., 2013). When accumulating in large amounts in sediments, these elements, most of which are toxic, are known to cause irreversible changes in the structure of organisms inhabiting the sediments and then to migrate upwards in the trophic chain, whose top level may be occupied by humans (Liu et al., 2014; Moiseenko, 2015).

Thus, environmental geochemical studies of sediments in the small lakes in the north of Russia, including Karelia, are undeniably relevant. The purpose of this study was to provide a detailed environmental and geochemical assessment of the recent sediments in two small lakes – Liunkunlampi and Raivattalanlampi – in the Lahdenpohja District in southwestern Karelia The objectives of this study were to measure the accumulation of Pb, Cd, Tl, Sb, Sn, Zn, Cu and Bi in the core samples of recent sediments from the studied lakes; to give an overall assessment of the pollution level in the lakes, using total pollution (Z_c) as a measure; to identify the main fractions of heavy metals in the sediments and identify the role of organic matter in the sediments in Karelia in the accumulation of heavy metals; and to compare the pollution level in the two water bodies. The scope of the study covers the southwest of Karelia (Russia) and touches on environmental problems in northern Europe.

2. Material and methods

2.1. Description of the study area

The Lahdenpohja District is an administrative unit of the Russian region of Karelia, covering an area of 2,200 km^2, with its administrative centre in the town of Lahdenpohja (Fig. 1). The district extends along the northwestern coast of Europe's largest body of water, Lake Ladoga, and is located 150 km from Russia's second largest city, St Petersburg. In the north, the Lahdenpohja District borders Sortavala.

The terrain of the region is composed of Precambrian crystalline rocks and is the development area of the Ladoga series of Lower Proterozoic formations, found only in this area. The Ladoga series of rocks consists of biotite and mica schists and gneisses, or less frequently quartzite schists, as well as quartzites and conglomerates. Almost all the rocks in this region have undergone folding, metamorphism and large-scale granitization processes. Small bodies contain intrusive structures composed of gabbros and plagiogranites (Svetov and Sviridenko, 2005). The Quaternary deposits of the region formed after a glacier melted 10-12,000 years ago. Glacial, water-ice, lacustrine and sedimentary deposits are particularly evident here. The most widely developed deposits in the region are lake-glacial deposits, represented by varved clay and sands (Sinkevich and Ekman, 1995).

The district's hydrographic network drains entirely into Lake Ladoga. About 300 lakes are found here, most of them drainless or with an extremely low flow. Lake sediments, also called sapropel or gyttia, are usually represented by dark brown, green brown, green or black silt. The main components are organic matter, Si, Al and Fe. As a result of a lack of carbonate rocks in the area, water and sediments of water bodies, including lakes, have a low content of Ca in comparison with regions located further south of Karelia. Despite this characteristic, the sediments of Karelia can be useful for agriculture, medicine and environmental protection (Sinkevich and Ekman, 1995; Stankevica et al., 2012).

There are no large industrial enterprises in the territory of the Lahdenpohja District that could be linked to heavy metal emissions. In the only city in the district (Lahdenpohja), there is only a plywood factory and a logging company, as well as factories for baking and alcohol products. The federal automobile road A-121 runs from St Petersburg to Sortavala, and local branches of the October railway run through the district. Lake Liunkunlampi (61° 29'56.86" N, 29° 52'38.29" E) is a small water body with a surface area of 0.1 km^2, located 17 km from Lahdenpohja and 170 km from St Petersburg. The lake has a rounded shape. The catchment area of Lake Liunkunlampi (Fig. 1) includes only swamp and forest. There is no visible surface flow from the lake. Lake Raivattalanlampi (61° 14'33.07" N, 29° 39'20.86" E) is a small water body with a surface area of 0.4 km^2, located 42 km from Lahdenpohja and 140 km from St Petersburg. The lake has an elongated shape running from the northwest to the southeast. The small Hitola community is located nearby. The banks are made of solid pre-Quaternary rocks, and the littoral zone is waterlogged. There is no visible surface flow from the lake. In addition, the catchment area of Lake Raivattalanlampi includes the asphalt road and a section of railway with a railway station (Fig. 1). The main parameters of the morphology of the lakes studied thus far are in Table 1.

2.2. Sampling process and analytical research

We carried out fieldwork in July 2018, using a Garmin Echomap Plus 42cv echo sounder chartplotter to measure the depths of the lakes. We conducted echo sounder data processing and depth mapping in Golden Software Surfer 13. In both lakes, we sampled the sediments from an inflatable boat. We collected samples in the central part of the lakes – the accumulation zone – after depth sounding. We collected two core samples of sediments from each of the lakes using a Limnos sampler; each of the cores was subdivided into layers 2 and 5 cm thick on the shore immediately after sampling.

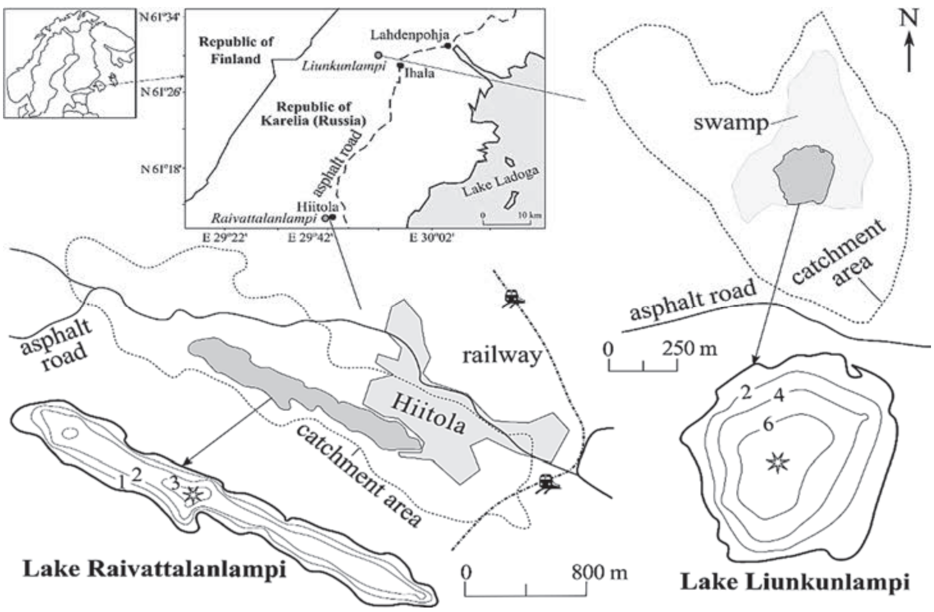

Fig. 1. Study area and maps of the depths of studied lakes

Then we placed the samples in plastic containers, which were labeled and packed in a cooler bag. We delivered the samples to a laboratory, where, after measurement of the pH of the sediments using a pH-420 millivoltmeter and an ESK-10610 glass-combined electrode, the samples were placed in a laboratory refrigerator, where they remained until dry, at a temperature of 4°C.

For further study, we dried the sediments samples to an air-dry point at room temperature and then to an absolutely dry point in an oven at a temperature of 110°C. We conducted the laboratory tests at the Analysis Center of the Institute of Geology at the Karelian Research Center, Russian Academy of Sciences in Petrozavodsk, Karelia, and at the Institute of Chemistry and Technology of Rare Elements and Minerals at the Kola Research Center, Russian Academy of Sciences in Apatity, Murmansk Region. We measured the trace element content in the sediment samples by the mass spectral method, using an XSeries-2 ICP-MS instrument from Thermo Ficher Scientific. Trace element concentrations are given in mg/kg (milligrams per kilogram). We presented a more detailed description of the sediment sample preparation technique in an earlier study (Slukovskii and Svetov, 2016).

To identify the various fractions of heavy metals in the core samples of lake sediments subdivided into 5-cm layers, we used the method of sequential extraction of fractions of elements from soil samples (Tessier et al., 1979), including identification of the following:

- water-soluble fractions (reagent H_2O);
- available (exchangeable) fractions (reagent NH_4CH_3COO);
- fractions bound to Fe and Mn hydroxides (reagents 0.04 M NH_2OH*HCl in 25% CH_3COOH);
- fractions bound to organic matter (reagents 0.02 M HNO_3 + 30% H_2O_2 and 3.2 M NH_4CH_4COO in 20% HNO_3);
- acid-soluble (residual) fractions (reagent HNO_3), and
- mineral (silicate) fractions obtained by deducting the combined concentration of all the above fractions from the total concentrations.

We decomposed the sediment samples to determine the total concentrations of heavy metals in the sediments in the core samples, subdivided into 2 cm layers by an acid breakdown using HF, HNO_3 and HCl in an open system. We performed statistical processing of the data in Microsoft Excel 2007.

Table 1. Main parameters of morphology of studied lakes

		Lake Liunkunlampi	*Lake Raivattalanlampi*
Coordinate		61°29'56.86" N, 29°52'38.29" E	61°14'33.07" N, 29°39'20.86" E
Square of lake, km^2		0.1	0.4
Square of catchment area, km^2		1.1	4.6
Coastline, km		0.85	4.53
Lake volume, km^3		0.00036	0.001
Lake length, km		0.29	2.06
Width, km	average	0.25	0.23
	maximum	0.20	0.29
Depth, m	average	3.6	2.5
	maximum	6.8	3.3

We designed Figures illustrating the results in EasyCapture 1.2.0 and Inkscape 0.48.4. We calculated total pollution index Z_c of the sediments by the formula in Eq. (1):

$$Z_c = \sum K_c - (n-1) \quad (1)$$

where K_c is the concentration coefficient, calculated as the ratio of the concentration of the metal in the sample to the background concentration of the element, and n is the number of metals whose concentrations exceed the background values (Akhtyamova et al., 2012; Slukovskii, 2015). There are four pollution levels, according to the total pollution index Z_c: low ($Z_c < 16$), moderate ($16 < Z_c < 32$), high ($32 < Z_c < 128$) and extremely high ($Z_c > 128$).

The geoaccumulation index (I_{geo}) of heavy metals in bottom sediments was calculated using the formula in Eq. (2):

$$I_{geo} = \log_2\left(\frac{C}{1.5 * B}\right) \quad (2)$$

where C is the metal concentration in a given layer, and B is the background metal concentration measured in the deepest layer of each sediment core (Müller, 1979). There are six pollution levels, according to the total pollution index I_{geo}: uncontaminated ($I_{geo} \leq 0$), uncontaminated to moderately contaminated ($0 < I_{geo} < 1$), moderately contaminated ($1 < I_{geo} < 2$), moderately to heavily contaminated ($2 < I_{geo} < 3$), heavily contaminated ($3 < I_{geo} < 4$), heavily to extremely contaminated ($4 < I_{geo} < 5$) and extremely contaminated ($Z_c > 5$).

3. Results and discussion

A bathymetric survey of Lakes Liunkunlampi and Raivattalanlampi revealed that the depressions of both lakes have a simple structure, with the greatest depths in the central parts. The maximum depth of Lake Liunkunlampi is 6.8 m, and its average depth is 3.6 m. Because the lake is surrounded by a bog, Liunkunlampi has no littoral zone as such, and we often measured depths greater than 1.5 m right at the shoreline. The maximum depth of Lake Raivattalanlampi is 3.3 m, and its average depth is 2.5 m. Despite the length of the lake, which is about 2 km, there were almost no depth differences along the central axis of the water body. The lake's littoral zone is made up of either sandy beaches or rock outcrops that have gradually become buried under the sediments; therefore, there are no extreme variations in depth near the shore.

The sediments are dark brown (Lake Liunkunlampi) and greenish-brown (Lake Raivattalanlampi) silt. The greenish-brown silt from Lake Raivattalanlampi is denser than the dark brown sediments in Lake Liunkunlampi; therefore, the core samples from the two lakes differ in thickness – under the action of gravity, the Limnos sampler could penetrate only the top 34 cm of sediments in Lake Raivattalanlampi. This is explained by the fact that the sediments are of the organosilicate type, containing up to 26% organic matter as such (Mikhailov and Aminov, 2006). In Lake Liunkunlampi, the sediments are softer because it belongs to the organic type, with organic matter content of up to 88% (Mikhailov and Aminov, 2006). The sediments of Lake Liunkunlampi probably have more organic matter than those of Lake Raivattalanlampi, due to differences between the catchment areas of the lakes. Lake Liunkunlampi is surrounded by swamp and forest, but Lake Raivattalanlampi has banks made of solid pre-Quaternary rocks.

There are also differences in pH in the sediments from the two lakes. In Lake Liunkunlampi, the sediments have an acidic reaction, with a pH between 5.11 and 5.57 pH; values tend to grow with depth in the core samples. In Lake Raivattalanlampi, the sediment is slightly acidic, with a near-neutral pH of 6.30 to 6.55. The lowest pH values are observed in the middle part of the core samples. These differences can be explained by the higher content of organic matter in the sediments of Lake Liunkunlampi compared with Lake Raivattalanlampi.

According to an another study based on an analysis of ^{210}Pb radioactivity in the sediment core of Lake Ukonlampi, located near Lakes Liunkunlampi and Raivattalanlampi, the medium rate of accumulation in lakes of the southwestern Republic of Karelia during recent (industrial) times has been about 1.3 mm per year (Slukovskii et al., 2020). These data are consistent with the results obtained in the study of modern deposits in lakes in Finland, Norway and the Murmansk Region of Russia (Dauvalter and Kashulin, 2010; Verta and Tolonen, 1989).

The average concentrations of heavy metals collected from sediment samples appear in Table 2. For Lake Liunkunlampi, low concentrations of Cu, Zn and Pb are evident. These findings were compared to the background level of metals found in small lakes in Norway. It is relevant to point out that the average content of Cd found in the sediments of Lake Liunkunlampi was slightly higher than in the Norwegian background level for Cd (Rognerud et al., 2000). A further finding was the enrichment of Lake Liunkunlampi sediments containing Cd and Pb by comparison with the background level of these metals found in small lakes in the Murmansk region in the Arctic zone of Russia (Dauvalter, 2012). However, the average content of heavy metals, with the exception of Cd, Sb and Bi, found in the sediments of Lake Liunkunlampi is lower than that in the studied elements in continental Earth's crust (Wedepohl, 1995).

For Lake Raivattalanlampi, the concentrations of all studied metals are higher than their concentrations in continental Earth's crust (Wedepohl, 1995). Moreover, the content of Cu, Zn, Cd and Pb in the sediments of Lake Raivattalanlampi is higher than the background levels of these metals in small lakes in Norway, as well as the background levels of these metals in small lakes of the Murmansk Region (Dauvalter, 2012; Rognerud et al., 2000). Data from study of the lakes of Siberia have confirmed this observation; there, preindustrial sediments of the organosilicate type are usually more enriched with metals than preindustrial sediments of the organic type (Strakhovenko, 2011).

An analysis of the vertical distribution of the total concentrations of heavy metals in the core samples from the two lakes revealed both the general patterns of accumulation of chemical elements and the differences in environmental geochemistry between the sediment samples from the two different water bodies. The similarity is linked to a single set of elements with elevated concentrations in the upper parts of the core samples and to the vertical distribution thereof along the sediment cores (Figs. 2 and 3).

All these elements are the most common geochemical agents of long-range transport for pollutants (Michinobu et al., 2013; Rognerud and Fjeld, 2001; Stankevica et al., 2012). Some of these, especially Pb, Cd, Sb, Cu, Zn and Tl, pose a significant threat to living organisms because they have pronounced toxic properties (Denisov, 2007; Esmaeilzadeh et al., 2016; Liu et al., 2014; Moiseenko, 2015). According to numerous studies, these elements can be carried by aerosols over tens, hundreds and even thousands of kilometres (Bartnicki, 1994; Johansson et al., 2001; Vinogradova et al., 2017). The total annual incoming transport of these metals into Karelia by air is estimated at 1.5 tons (Vinogradova et al., 2017).

The bulk of heavy metals in the emissions are Pb, Cu, Ni and Cd (Vinogradova et al., 2017). According to available data (Vinogradova et al., 2017), the northern (33%), western (27%) and southern (24%) air masses that carry heavy metal impurities mainly fall in the territory of Karelia. Thus, the largest sources of pollution are the neighbouring territories of Finland, Norway, the Murmansk Region, Leningrad Oblast and St Petersburg (Dauvalter, 2012; Moiseenko, 2015; Rognerud and Fjeld, 2001; Vallius and Leivuori, 2003). With the exception of the influence of transport, no large local sources of pollution exist because both lakes lie in a relatively pristine forested landscape.

Table 2. Descriptive statistics of heavy metal concentrations of sediments from studied lakes and data of background levels of heavy metals in lakes sediments of neighboring regions (Norway (B_{NOR})* and Murmansk region (B_{MR}))** and in the Continental Crust (CC)***

	Lake Liunkunlampi			*Lake Raivattalanlampi*			B_{NOR}	B_{MR}	*CC*
	Median	*Range*	*V, %*	*Median*	*Range*	*V, %*			
Cu	12.3	9.6-21.7	27	34.6	30.5-42.9	13	19.5	28.0	25
Zn	45.1	38-148	52	123	108-169	16	87.0	94.0	65
Cd	0.43	0.25-2.05	82	1.38	0.96-1.98	21	0.26	0.20	0.1
Sn	0.57	0.40-4.04	97	2.91	1.68-4.08	32	n/d	n/d	2.3
Sb	0.35	0.09-1.97	102	0.66	0.35-1.06	38	n/d	n/d	0.3
Tl	0.07	0.05-0.23	55	0.70	0.48-0.84	18	n/d	n/d	0.52
Pb	14.1	3.3-85.1	107	30.0	17.7-47.4	35	24.5	4.0	14.8
Bi	0.12	0.07-0.75	98	0.70	0.45-4.06	83	n/d	n/d	0.09

*Note. *(Rognerud et al., 2000), **(Dauvalter, 2012), ***(Wedepohl, 1995). Range - minimum and maximum values of concentration, V is a coefficient of variation, B – background level of heavy metals.*

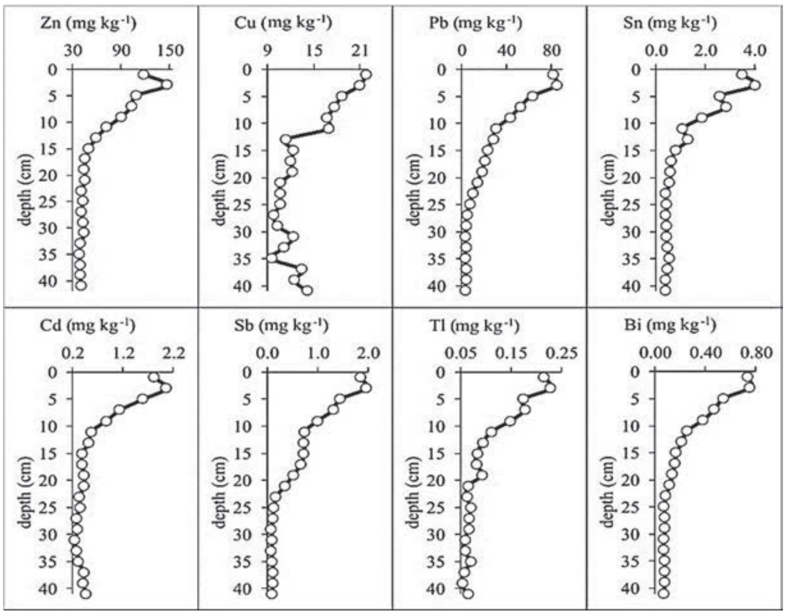

Fig. 2. Vertical distribution of heavy metal concentrations in sediment core of Lake Liunkunlampi

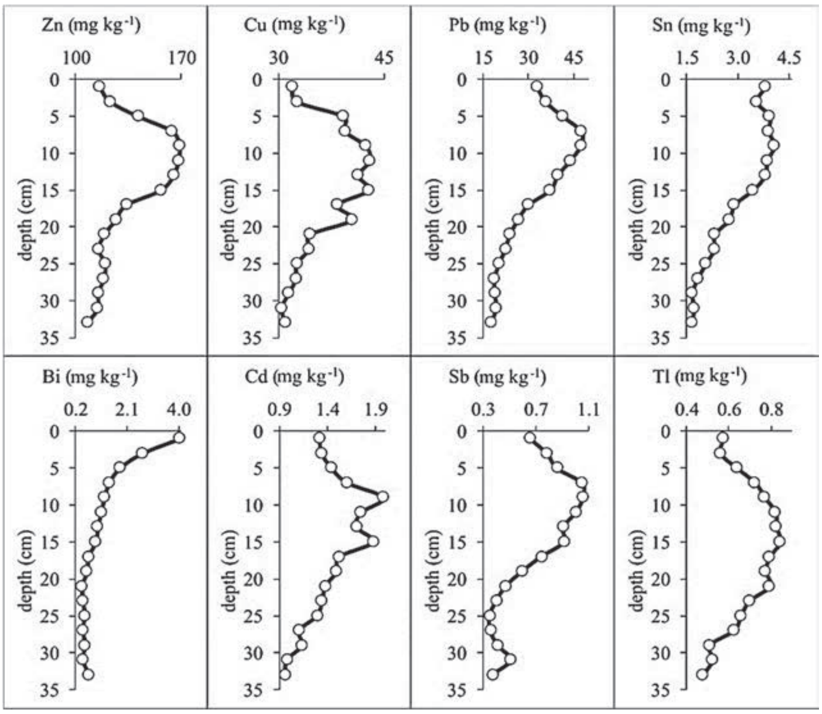

Fig. 3. Vertical distribution of heavy metal concentrations in sediment core of Lake Raivattalanlampi

Therefore, long-range transport is the main source of pollutants entering the ecosystems of the studied lakes. St Petersburg is a major source of pollution, given that its anthropogenic impact has a significant effect on the formation of geochemically abnormal levels of Cu, Zn, Ni, Cr, Pb, Cd, Co, Mo, Mn, Fe, Ba and Hg in the sediments in the city's small water bodies and in the Gulf of Finland in the Baltic Sea (Vallius and Leivuori, 2003). To a certain degree, the environmental pollution in the study area in the southwest of Karelia is associated with long-range transport of pollutants from Finland – these are mainly metals originating from the emissions of smelters in the cities of Imatra and Kotka (Ukonmaanaho et al., 1998; Verta et al., 1998). The heavy metals entering the study area from anthropogenic sources are mainly Pb, Cd, Cu, Zn, Ni, Cr and Sb. It should be noted that in a Finnish study of a large number of small lakes, similar patterns arose in the behaviour of heavy metals in the recent sediments. A significant increase in the level of these elements above the background values in the upper layers of sediments, based on Pb^{210} and Cs^{137} isotope dating, started back in the early twentieth century, mainly as a result of long-range transport of pollutants from the industrially developed regions of Finland, Russia and the former USSR (Verta et al., 1998). Similar patterns also appeared in the upper layers (10–20 cm) of sediments in Lake Ladoga, whose catchment area includes the studied small lakes Liunkunlampi and Raivattalanlampi and where a recent trend towards higher concentrations of Pb, Cu and Zn is evident (Davydova et al., 1999).

Thus, it is obvious that the concentration peaks of heavy metals found in recent sediments in the Lahdenpohja District of Karelia are of anthropogenic origin. Figs. 2 and 3 show that the absolute total concentrations of some metals differ. For instance, in the lower (background) layers of the core sample of the recent sediments from Lake Raivattalanlampi, concentrations of all elements are noticeably higher than in similar sediment layers in Lake Liunkunlampi. The fact that there are different types of sediments in the two water bodies explains this, because organosilicate sediments tend to contain more trace elements than organogenic sediments (Gaskova et al., 2017). This is due to the predominance in organosilicate sediments of terrigenous fractions, compared with purely organic sediments. Conversely, with the increasing role of the anthropogenic factor in the sediment geochemistry of the studied lakes in the southwest of Karelia, the situation may change significantly. The presence of Cd, Sb and Pb, in particular, illustrates this: Their concentrations in the uppermost layers of the sediment samples from Lake Liunkunlampi are noticeably higher than in those from Lake Raivattalanlampi (Figs. 2 and 3). In this case, organic matter, whose content is higher in the sediments from Lake Liunkunlampi, acts as a sorbent of metals coming from anthropogenic sources (Förstner et al., 2004). Thus, this lake acts as a sink for heavy metals. Close correlation exists between almost all the metals studied in the bottom sediments. The closest bonds were found in the Cu–Zn, Cu–Tl, Zn–Cd, Zn–Sn, Cd–Sn and Sb–Pb pairs ($R > 0.9$ at $p < 0.01$). The correlation coefficients among the remaining elements appear in Table 3. The obtained patterns indicate a unified model of the supply and accumulation of these heavy metals in the columns of bottom sediments in small lakes in the southwest region of Karelia. It should be noted that earlier similar patterns were established for Lake Ukonlampi, located in the same region of Karelia (Slukovskii et al., 2020).

Table 3. The correlation matrix of heavy metal concentrations from sediments of Lakes Liunkunlampi and Raivattalanlampi, Karelia

	Cu	*Zn*	*Cd*	*Sn*	*Sb*	*Tl*	*Pb*
Zn	0.93**						
Cd	0.84**	0.96**					
Sn	0.82**	0.94**	0.95**				
Sb	0.34*	0.63**	0.74**	0.75**			
Tl	0.98**	0.88**	0.79**	0.76**	0.25		
Pb	0.40*	0.69**	0.80**	0.80**	0.99**	0.32*	
Bi	0.58**	0.58**	0.55**	0.72**	0.34*	0.54**	0.40*

Note. The critical level of correlation significance: $^{*}R_{crit}=0.32$ *for* $p<0.05$ *and* $^{**}R_{crit}=0.41$ *for* $p<0.01$

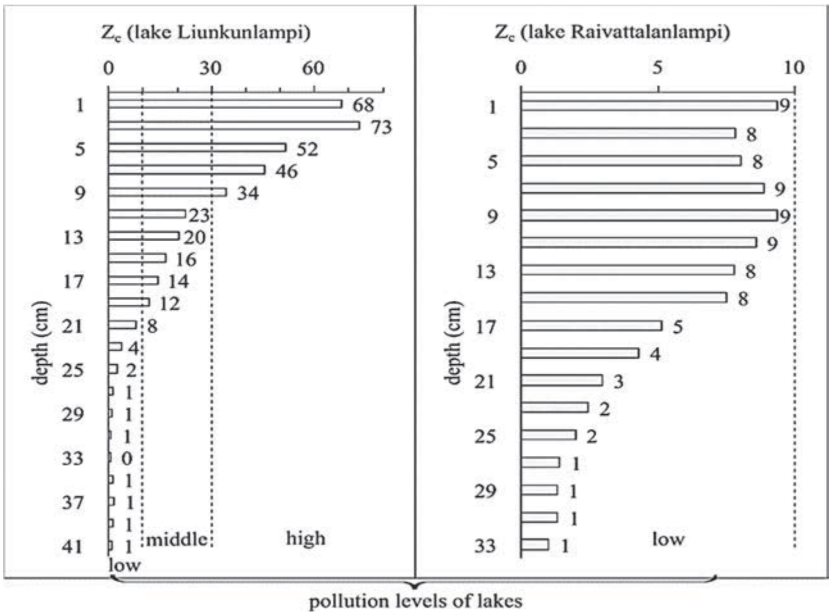

Fig. 4. Values of the total pollution index (Zc) calculated by Eq. (1) in different layers of recent sediments of the lakes of Liunkunlampi and Raivattalanlampi

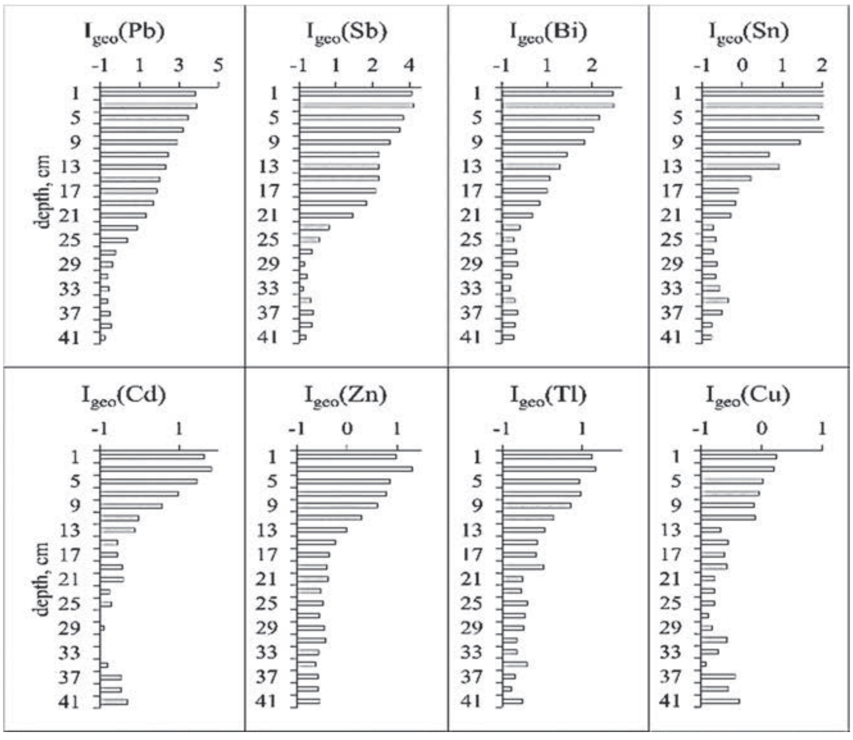

Fig. 5. Values of the geo-accumulation index (Igeo) of heavy metals in the sediments of Lake Liunkunlampi

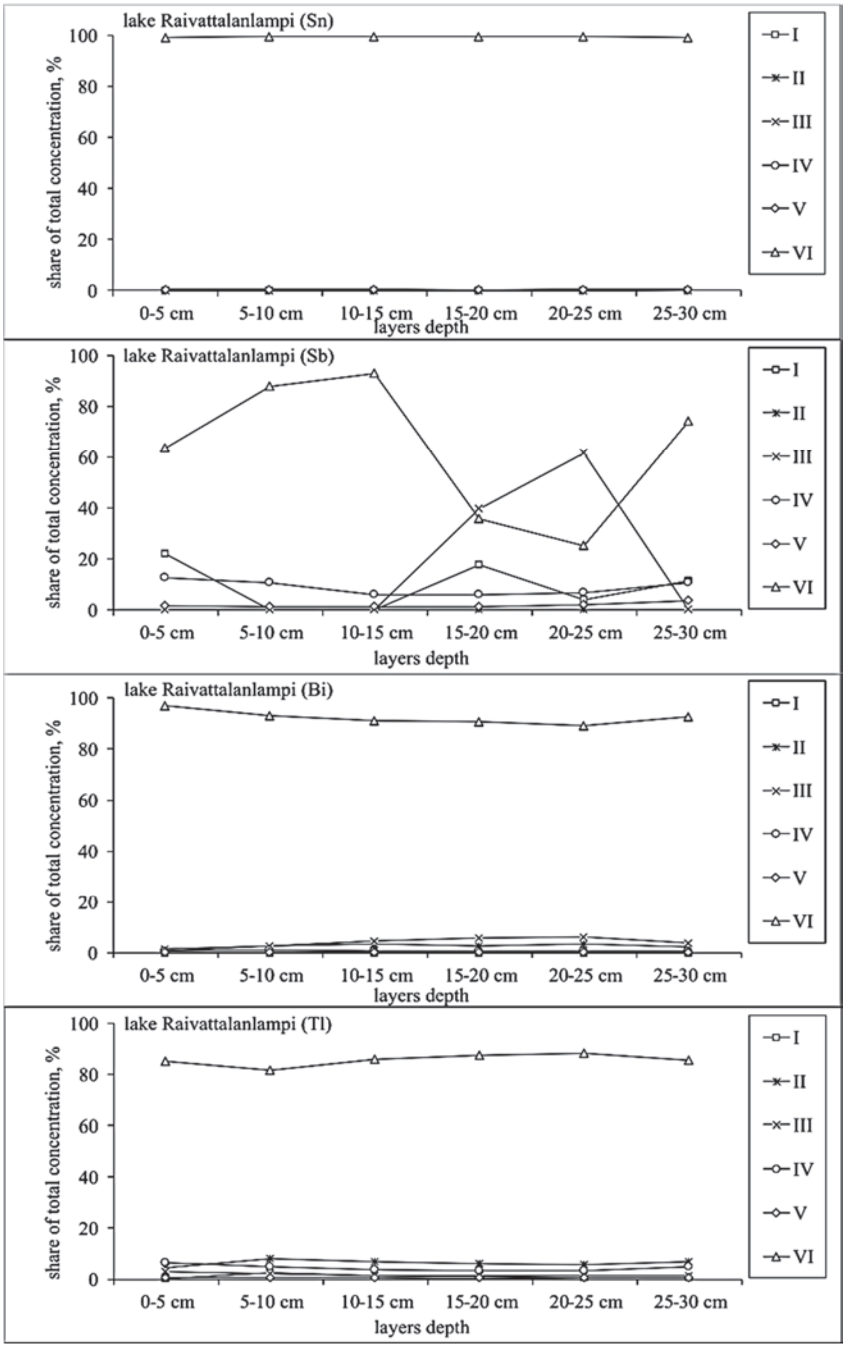

Fig. 6. Share of different fractions of heavy metals (Sn, Sb, Bi, Tl) in sediments of lake Raivattalanlampi. Note: I - water-soluble fractions, II - available (mobile) fractions, III - fractions bound to hydroxides Fe, IV - fractions bound to organic matter, V - acid-soluble (residual) fractions, VI - mineral (silicate) phase

Due to the fact that the organic upper layers of the sediments from Lake Liunkunlampi were significantly different from the background layers in terms of their heavy metal content compared with the organosilicate sediments from Lake Raivattalanlampi, where the difference is not so pronounced, the two lakes have different levels of metal pollution based on the total pollution index calculated with Eq. (1) (Fig. 4). The uppermost layers of the sediments from Lake Liunkunlampi (0–10 cm) display a high level of pollution, the intermediate layers (10–20 cm) a moderate level and the underlying layers (20–42 cm) a low level. In contrast, the sediments from Lake Raivattalanlampi has a low pollution level irrespective of depth. The key factor here is the accumulation of organic matter as pollutants enter the lakes from the outside.

Analysis of the geoaccumulation index (I_{geo}) of heavy metals in the sediments of studied lakes has also revealed that the sediments of Lake Liunkunlampi are more contaminated than those of Lake Raivattalanlampi. For example, the upper layers of Liunkunlampi sediments were moderately to heavily contaminated by Pb, Sb, Sn and Bi (I_{geo} values from 2 to 4) (Fig. 5). Besides, for Zn, Cd and Tl in the 0–6 cm layer, there was a moderate level of contamination in Lake Liunkunlampi. In the lower 8–42 cm layer of the sediments, there was an uncontaminated pollution level of Ukonlampi Lake. There was similar behaviour of I_{geo} values for sediments from the urbanised areas of Karelia (Medvedev et al., 2019). On the other hand, according to the calculations of the geoaccumulation index (I_{geo}), the sediments of Lake Raivattalanlampi have both the uncontaminated level and the uncontaminated to moderately contaminated level for all metals, except Bi, which has I_{geo} values ranging from 1 to 3 in the upper sediment layers.

Fraction analysis of the heavy metals in the sediments from Lakes Liunkunlampi and Raivattalanlampi supports the observed patterns. For example, in the sediments from Lake Raivattalanlampi, almost all metals are largely in the mineral phase, which is especially true for Sn (up to 99% of the total content), Bi (89–97%) and Tl (81–89%) (Fig. 6). Metals most strongly bound to the organic matter in the sediments from Lake Raivattalanlampi are Cu (30–54%) and Zn (13–24%), while Cd, Sb and Pb are bound less strongly and Sn, Tl and Bi are weakly bound (Figs. 6 and 7). Metals such as Zn, Cd and Pb bind well to iron hydroxides (Fig. 7). The share of such zinc fractions in the total concentration is up to 20%, of cadmium up to 13% and of lead up to 12%. The same elements plus Tl were mobile in the sediments from Lake Raivattalanlampi (Fig. 6). The most mobile were Zn (up to 22% of the total content) and Pb (up to 26%). Zinc, cadmium, antimony and thallium also have the highest concentrations of water-soluble fraction (Fig. 7).

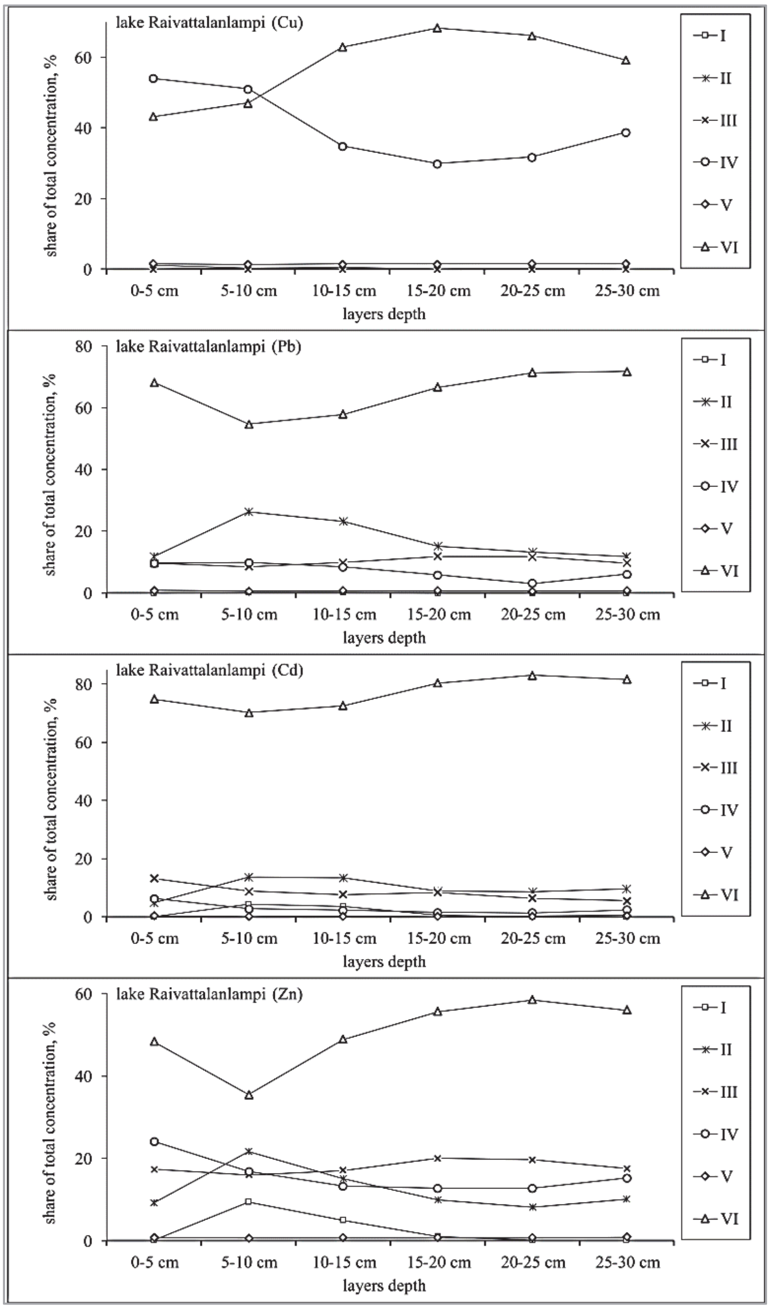

Fig. 7. Share of different fractions of heavy metals (Cu, Zn, Cd, Pb) in sediments of lake Raivattalanlampi. Note: I - water-soluble fractions, II - available (mobile) fractions, III - fractions bound to hydroxides Fe, IV - fractions bound to organic matter, V - acid-soluble (residual) fractions, VI - mineral (silicate) phase

In the sediments from Lake Liunkunlampi, the dominant fraction for a number of metals is the organic one (Figs. 8 and 9). This is especially pronounced in the accumulation in the sediments of Cu (55–95% of the total content), Zn (up to 61%), Cd (up to 30%), Sn (up to 48%), Sb (up to 97%) and Bi (up to 68%).

A significant amount of Sn and Tl and some of the other metals are retained in the mineral phase, though mainly in the uppermost layer of the sediments (0–5 cm) (Fig. 9). Zn (10–61%), Cd (10–62%) and Pb (7–31%) are most closely bound to Fe compounds (Fig. 8).

Significant levels of the same metals plus Tl are found in the mobile fraction: Zn (up to 26%), Cd (up to 36%), Tl (up to 22%) and Pb (up to 49%). The mobile fraction contains no Cu, Sn or Sb (Figs. 7 and 8). Thus, as a result of the large share of organic matter in the sediments in Lake Liunkunlampi, many metals tend to bind to the organic matter, compared with the sediments in Lake Raivattalanlampi, in which the mineral fraction (even for Cu) is dominant.

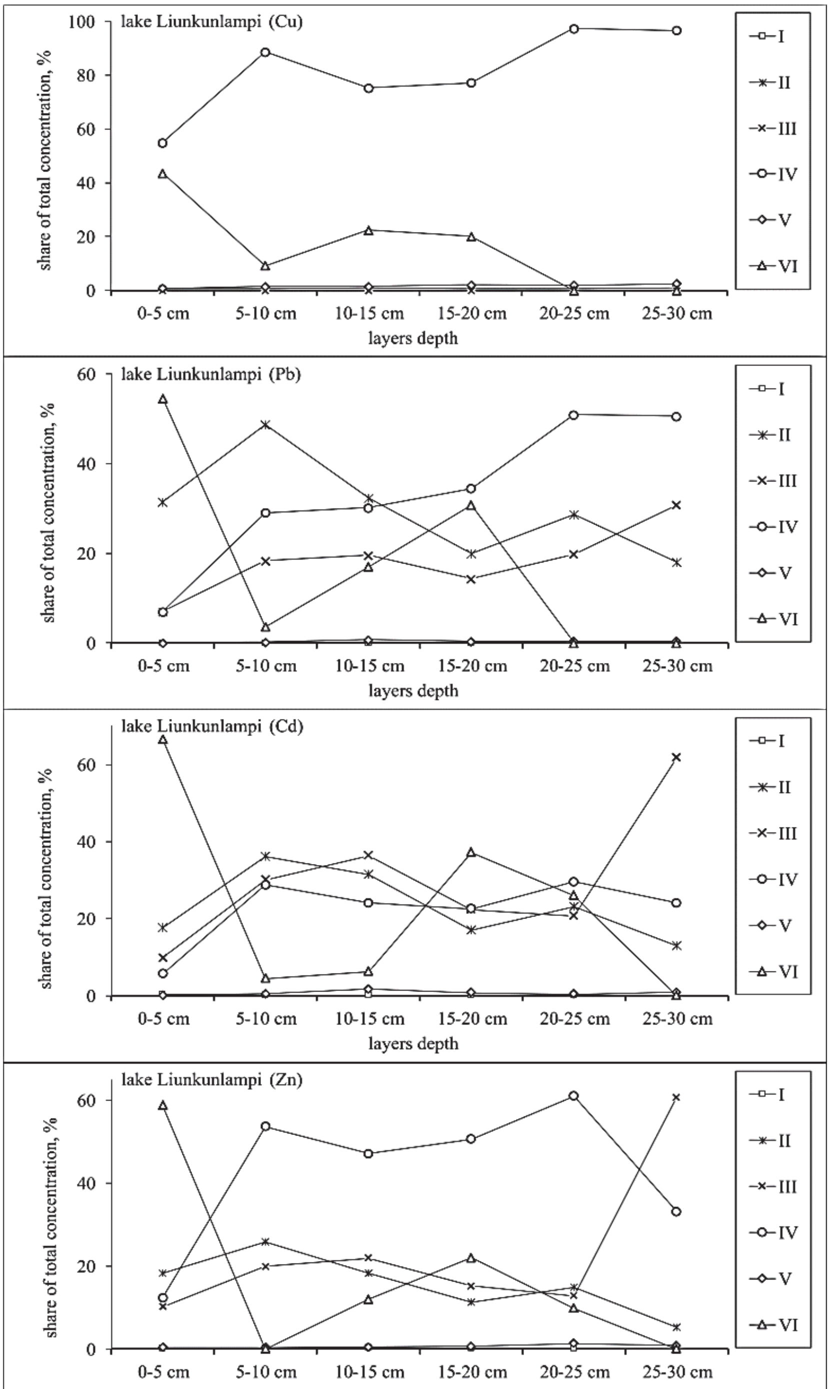

Fig. 8. Share of different fractions of heavy metals (Cu, Zn, Cd, Pb) in sediments of lake Liunkunlampi. Note: I - water-soluble fractions, II - available (mobile) fractions, III - fractions bound to hydroxides Fe, IV - fractions bound to organic matter, V - acid-soluble (residual) fractions, VI - mineral (silicate) phase

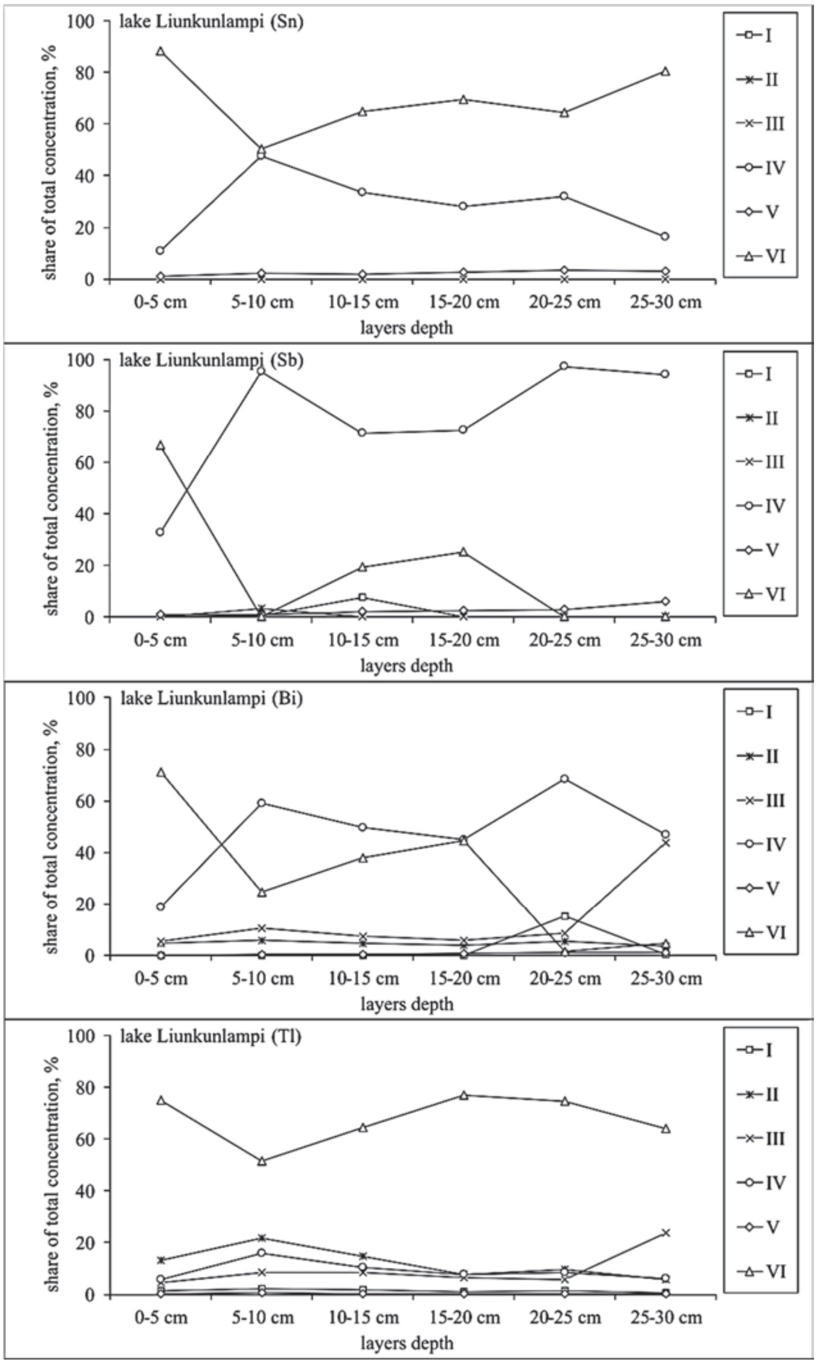

Fig. 9. Share of different fractions of heavy metals (Sn, Sb, Bi, Tl) in sediments of lake Liunkunlampi. Note: I - water-soluble fractions, II - available (mobile) fractions, III - fractions bound to hydroxides Fe, IV - fractions bound to organic matter, V - acid-soluble (residual) fractions, VI - mineral (silicate) phase

The observed patterns are consistent with the findings of other studies of sediments in freshwater lakes (Förstner et al., 2004; Li et al., 2001; López et al., 2010). These and other papers highlight the key role of organic matter in the accumulation of heavy metals in aquatic environments exposed to anthropogenic impact. This circumstance is a major prerequisite for the migration of heavy metals up the trophic pyramids (sediment – benthos – fish) of the studied and similar water bodies as well as those located in the southwestern part of Russian Karelia. It is important to note that a number of metals, primarily Pb, Cd, Zn and Tl, are significantly mobile in the sediments of both the studied lakes, which can cause secondary pollution of the aquatic environment when the physicochemical conditions in the water body change (Li et al., 2001). The findings of this study can be extremely useful in assessing the recreational potential of small lakes in the southwestern part of Karelia and in the development of the sapropel reserves of the studied sediments. It is recommended to reject the most contaminated upper layer of sediments to prevent heavy metals from entering fertilizers and feed supplements to be produced. Currently, Pb levels in Lake Liunkunlampi, the most promising of the two studied lakes, exceed the existing regulatory standards for sapropel (Mikhailov and Aminov, 2006). Unfortunately, similar patterns exist in many lakes in the southern part of Karelia (Medvedev et al., 2019; Slukovskii et al., 2020).

4. Conclusion

The environmental and geochemical study of the sediment in the lakes of the southwestern part of the Republic of Karelia, with Lakes Liunkunlampi and Raivattalanlampi as representative cases, demonstrated the following:

- The main pollutants of small drainless or low flow lakes in the study area are heavy metals such as Pb, Cd, Zn, Cu, Sb, Sn, Bi and Tl. The highest levels of these elements were found in the uppermost layers of the studied core samples of recent sediments – between 0 and 15 cm.
- The main pollution factor of Lakes Liunkunlampi and Raivattalanlampi, located in a forested boggy landscape with close to background pollution levels, is long-range transport of pollutants from neighboring regions in Russia and other European countries. Similar patterns in the vertical distribution of heavy metals in sediments exist in Russia's Murmansk Region, Finland and other regions.
- The main fractions controlling the accumulation of heavy metals in sediments are mineral and organic fractions. With an increase in the share of organic matter in sediments, its ability to accumulate pollutants increases. Therefore, the sediments in Lake Liunkunlampi, which contains more organic matter, is more polluted than that in Lake Raivattalanlampi, where the share of organic matter is significantly lower.
- Metals such as Cu, Zn, Cd, Sb and Pb are most strongly bound to the organic matter in the sediments from the two studied lakes. In addition, a large proportion of mobile fractions of Zn, Cd, Tl and Pb was found in the lakes, which may have a negative impact on aquatic life and lead to a deterioration in the environmental status of water bodies in the event of secondary pollution of the aquatic environment.

The study not only answers important questions of theoretical science but can also be of use if the water bodies of the southwest of Karelia are considered for management for recreational and/or industrial (as a source of water or sapropel) purposes.

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