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# Background concentrations of heavy metals and other chemical elements in the sediments of small lakes in the south of Karelia, Russia

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Key words: sediments, small lakes, background concentrations of elements, heavy metals, the Republic of Karelia Abstract

The average background concentrations of 42 elements, including heavy metals which are the most dangerous pollutants of the environment, were calculated based on detailed research of sediments of 15 small lakes in the south of the Republic of Karelia. The sediment samples from the lakes were collected from 2016 to 2018. The main items of equipment were a gravity sampler Limnos and hand sampler. The former is capable of producing a 60 cm core and dividing it into 1 cm layers, the latter can enter sediment to a depth of 15 m. All samples were prepared by chemical analysis and measured using uniform methods. The concentrations of chemical elements were taken by the mass-spectral method on a XSeries-2 ICP-MS. To reveal the layers accumulated in the pre-industrial period, similar research of the area of the Murmansk region and countries of the Scandinavian Peninsula were used. Besides this, the geochemistry and geochronology of lake studies of the author were also used. Eventually, from 73 to 76 samples were taken for an assessment of background concentrations of heavy metals and other elements in the sediments of the lakes from Karelia's south. Given that the data obtained do not obey the normal distribution law, which is often found in geochemistry, the median sample was taken as the averaged background concentration of chemical elements. The results were similar to analog data for neighboring regions, including the Murmansk region and Scandinavian countries. Moreover, the levels of accumulation of chemical elements in lake sediments of Karelia's south are similar to some of the data for stream sediments of the studied region. The exceptions were elements controlled by terrigenous fractions of the stream sediments. This fraction is more rapidly accumulated in the stream and river sediments than in lake sediments. New data can be used for future environmental and geochemistry studies of the sediments of small lakes subject to anthropogenic impact.

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# Оценка фоновых концентраций тяжелых металлов и других химических элементов в донных отложениях малых озер юга Карелии

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Реферат

На основе детального исследования донных отложений 15 малых озер южной части Республики Карелии были рассчитаны усредненные фоновые значения 42 элементов, в том числе тяжелых металлов как наиболее опасных загрязнителей окружающей среды. Полевые работы, включающие отбор проб донных отложений, проводились в период с 2016 по 2018 гг. Основными инструментами отбора служили пробоотборник Limnos, позволяющий получить колонки донных отложений высотой до 60 см с последующим разделением на слои по 1 см, и ручной бур, способный отбирать пробы до 15-метровой глубины. Все образцы подготовлены и проанализированы по единой методике. Определение химических элементов осуществлялось при помощи масс-спектрометра с индуктивно-связанной плазмой ISP-MS. Анализ аналогичных исследований на территории Мурманской области и стран Скандинавского полуострова, имеющих сходные геологические условия с территорией Республики Карелии, а также анализ собственных геохимических и геохронологических данных позволил выделить слои донных отложений малых озер Карелии, образовавшиеся в доиндустриальный период развития общества. Общая выборка составила от 73 до 76 проб в зависимости от элемента. Учитывая, что полученные данные не подчиняются нормальному закону распределения, что нередко встречается в геохимии, за усредненные фоновые концентрации химических элементов принималось значение медианы выборки. Результаты близки к данным, ранее полученным для территорий соседних регионов, включая Мурманскую область и страны Скандинавского полуострова. Кроме того, установлено, что усредненные фоновые концентрации химических элементов в донных отложениях озер юга Карелии близки к усредненным фоновым концентрациям этих же элементов в осадках водотоков южной части республики. Исключения составляют литофильные элементы, которые в большей степени тяготеют к отложениям водотоков, где они контролируются терригенной составляющей речных осадков. Новые сведения можно использовать при дальнейших экологогеохимических исследованиях донных отложений малых озер, подверженных антропогенному

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#### Introduction

Studying the background concentrations of chemical elements, including those regarded as environmental pollutants, is an important component of environmental research ( $\mathcal{A}$ aybanbmep, 2012). In "classical" geology, averaged or reference concentrations of chemical elements are mainly used to normalize the concentrations of the respective elements in the studied matter, primarily in rocks and sediments ( $\mathcal{U}$ hmepnpemayus..., 2001). One example is the so-called clarke values, named after the American geochemist F. W. Clarke (1847–1931) and representing the average content of chemical elements in the Earth's crust, hydrosphere, the Earth, cosmic bodies, geochemical or cosmochemical systems, etc., relative to the total mass of the respective system. Normalization using clarke values reveals any abnormal concentrations of individual chemical elements, which is important in geological prospecting and commercial evaluation of mineral deposits (an applied task), as well as identifying the general patterns of migration and accumulation of chemical elements in geosystems (a theoretical task) ( $\mathcal{U}$ Oobau  $\mathcal{U}$ Op., 2011). Normalized concentrations of chemical elements are known as concentration factors or enrichment factors.

When studying environments capable of accumulating the incoming chemical elements (water, soil, bottom sediment (or just sediments) of water bodies, living organisms), clarke values are replaced by background concentrations, which may vary between regions. Background normalization makes it possible to identify abnormal concentrations of chemical elements caused by anthropogenic impacts on the environment (Даувальтер, 2012; Водяницкий, 2008). Based on background values, various indices and indicators can be calculated in the context of environmental and geochemical studies, which is aimed at an integrated assessment of the anthropogenic impact to characterize pollution levels and environmental damage caused. In this regard, background values are often compared with maximum permissible concentrations (MPC) in different standards or methodological guidelines. However, this comparison is not entirely correct, since standards are calculated taking into account the possible impact on living organisms, including humans, without taking into account regional geological and geochemical features, while background concentrations, on the contrary, emphasize these features without an explicit reference to any impact on the biotic components of the given environment. Considering that organisms, even those belonging to the same ecosystem, can respond very differently to anthropogenic impacts, as well as the fact that contemporary MPC tend to fail to take account of the regional climatic conditions and the adaptations that living organisms have developed, background concentrations seem to be a more reliable reference for standards governing the concentrations of chemical elements in soil, water, and sediments. Moreover, in the environmental interpretation of geochemical data, as opposed to the use of regulatory standards, it is advisable to take into consideration the behavior of living organisms themselves.

Currently, the most studied is the problem of background concentrations of chemical elements in the waters and soils in different regions of Russia and the world. The available research on the regional geochemistry of the sediments of water bodies is fragmented. Moreover, there are still no national regulatory standards for sediments, which in the absence of background values significantly complicate the interpretation of the collected geochemical data on the sediment of water bodies (Даувальтер, 2012). Adopting standards based on either background or normalized values estimated for soils, based on the clarke values of the Earth's crust or sedimentary rocks of the world can invalidate the results of environmental and geochemical studies. Thus, at present, the study of background concentrations of chemical elements in sediments is one of the most relevant research problems in environmental geochemistry and geoecological research. This problem is especially pressing in the northern regions of Russia with their abundance of rivers and lakes, where the key challenge facing environment limnologists and geochemists is to assess the present condition of water bodies taking into account the growing anthropogenic pressure on the environment around the world. One such region is the Republic of Karelia, a region of Russia with nearly 60 thousand lakes, most of which are small lakes (Kamanoz... 2001).

The aim of study is to estimate the background concentrations of chemical elements, including heavy metals (HMs), in the sediments of the small lakes in the southern part of the Republic of Karelia. This research problem has never been studied before in Russian Karelia.

## Materials and methods

Sediment sampling in 15 small lakes in the southern part of the Republic of Karelia (Fig. 1) took place in 2016–2018, both in summer and in late winter – spring. The five studied lakes are urban water bodies located in the cities of Petrozavodsk (Lakes Lamba and Chetyrekhverstnoe), Medvezhegorsk (Lakes Plotichie and Kitaiskoe), and Suoyarvi (Lake Kaipinskoe) (*Cηγκοβεκμά, 2018*). The other lakes are located mainly in forested or swampy forested areas at a distance from larger centers of population.

The samples were mostly collected using a Limnos sampler, allowing to extract stratified sediment core samples up to 60 cm long and separate these into 1 cm or thicker layers. Considering that sediments can differ in density and water content, the core samples ranged from 28 to 48 cm. In addition, in Lakes Lamba, Chetyrekhverstnoe, Gryaznoe, Rakhoilampi, and Dennoe, the sediment was drilled to the rock bed, silt, or clay, underlying the sediment. For this purpose, a manual drill (the so-called Russian drill) was used, which allows

drilling to a depth of 15 m, including water depth. Over the three years, 278 sediment samples were collected from various depths.

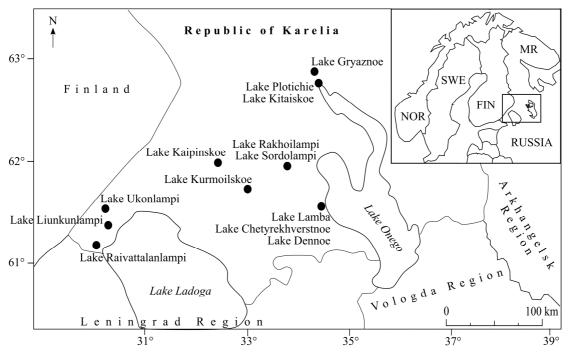


Fig. 1. Map of the study area. Inset: MR – Murmansk Region, NOR – Norway, SWE – Sweden, FIN – Finland Рис. 1. Карта района исследования.

Врезка: MR – Мурманская область, NOR – Норвегия, SWE – Швеция, FIN – Финляндия

All studied sediments are sapropel – the most common type of lake sediments in the Republic of Karelia (Синькевич и др., 1995). The proportion of organic matter in sapropel ranges between 15 and 90 %, however in the majority of the studied lakes, the sediments contained 40–50 % organic matter and can be classified as organic or organosilicate sediments. Only the sediments in Lake Lamba located in the city of Petrozavodsk (Слуковский и др., 2017) belongs to the organo-ferrous type, which is also often found in the region.

After collection, all samples were placed into plastic containers, which were labeled and packed in a cooler bag. Then the samples were delivered to the laboratory and placed in a refrigerator, in which they were stored until dry at a temperature of about 4 °C according to the methodological guidelines. For further study, the sediment samples were dried to an air-dry condition at room temperature and then to an absolutely dry condition in an oven at a temperature of approximately 105–110 °C. Laboratory tests were carried out at the Analysis Center of the Institute of Geology of the Karelian Research Centre of the Russian Academy of Science, in Petrozavodsk, Karelia.

Sediment samples were decomposed with acid in an open system. For analysis, sub-samples 0.1 g each were used. The samples were placed in 50 ml Teflon glasses, 0.1 ml of a solution containing 8 ppb 161 Dy was added (to monitor chemical yield during the decomposition of samples) and then several drops of deionized water. Then, 0.5 ml of HClO<sub>4</sub> (Perchloric acid fuming 70 % Supratur, Merck), 3 ml of HF (High Purity, TU 6-09-3401-88), 0.5 ml of HNO<sub>3</sub> (High Purity GOST 11125-84<sup>1</sup>) were added and evaporated until intense white vapor was observed. HF, HNO<sub>3</sub>, HCl underwent additional purification in a PTFE/PFA SubboilingEco IR distiller. The glasses were cooled, their walls were washed with water, and the solution was again evaporated to wet salts. Then, 2 ml of HCl (High Purity, GOST 14261-77<sup>2</sup>) and 0.2 ml of a 0.1 M solution of H<sub>3</sub>BO<sub>3</sub> (AR grade) were added and evaporated to a volume of 0.5–0.7 ml. The resulting solutions were transferred into polyethylene bottles and diluted with deionized water to 20 ml. For analysis, basic solutions diluted by a factor of 20 were used. To prepare blank samples, the above procedure was repeated in Teflon glasses without samples. Together with the analyzed samples, blank samples and one standard (control) sample (sediments from Lake Baikal BIL-1 – GSO 7126-94) were decomposed.

The content of chemical elements (Li, Sc, Ti, V, Cr, Mn, Co, Ni, Cu, Zn, Rb, Sr, Y, Zr, Nb, Mo, Cd, Sn, Sb, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu, Hf, W, Tl, Pb, Bi, Th, U) in the sediment samples was measured by the mass spectral method using an XSeries 2 ICP-MS instrument by Thermo Ficher

<sup>&</sup>lt;sup>1</sup> GOST 11125-84. Super pure nitric acid. Specifications. Moscow, 2006.

<sup>&</sup>lt;sup>2</sup> GOST 14261-77. Hydrochloric acid super pure. Specifications. Moscow, 1988.

Scientific. A total of 11 676 chemical element measurements was performed. Further analysis of the collected data taking into account the reference sample showed that the measured concentrations in mg/kg are characterized by a relative standard deviation (RSD) of 5.5–16.7 % and a correlation coefficient of  $R^2 = 0.997$  (Table 1). Thus, the relative measurement error did not exceed the permissible values for the chemical elements identified in this study, including HMs (*Csemos u dp.*, 2015).

Table 1. The results of chemical composition measurements in mg/kg of the certified standard BIL-1 by ICP-MS using an X-Series 2 quadrupole mass spectrometer by Thermo Fisher Scientific at Analysis Center of IG KarRC RAS in 2016–2018

Таблица 1. Результаты измерений химического состава (в мг/кг) сертифицированного стандарта BIL-1 ICP-MS с использованием масс-спектрометра X-Series 2 фирмы Thermo Fisher Scientific в Аналитическом центре ИГ КарНЦ РАН в 2016–2018 гг.

Element	DL	BIL-1 <sub>at.</sub>	±	BIL-1 <sub>meas.</sub> , $n = 32$	RSD <sub>abs.</sub>	RSD <sub>rel.</sub> , %
Li	0.24	37.00	4.00	40.33	2.56	6.3
Sc	8.9	13.00	2.00	16.00	2.35	14.7
Ti	5.5	n/a	n/a	3 712.47	406.88	11.0
V	3.1	110.00	10.00	106.19	10.69	10.1
Cr	2.5	66.00	4.00	66.24	6.18	9.3
Mn	0.46	n/a	n/a	3 110.09	274.90	8.8
Co	0.034	18.00	2.00	16.16	0.98	6.1
Ni	6.2	54.00	6.00	50.09	4.44	8.9
Cu	0.68	52.00	7.00	48.28	3.24	6.7
Zn	0.51	96.00	14.00	102.59	5.61	5.5
Rb	0.086	93.00	5.00	95.40	6.38	6.7
Sr	0.13	266.00	30.00	262.43	19.73	7.5
Y	0.1	30.00	4.00	23.59	1.52	6.5
Zr	0.22	156.00	13.00	89.43	12.11	13.5
Nb	0.02	12.00	2.00	10.69	1.04	9.8
Mo	0.1	2.90	0.50	3.53	0.37	10.6
Cd	0.01	n/a	n/a	0.32	0.05	16.5
Sn	0.21	3.20	0.50	2.85	0.48	16.7
Sb	0.024	0.95	n/r	0.84	0.12	14.3
Cs	0.005	6.00	1.00	5.63	0.42	7.5
Ba	4.3	710.00	70.00	698.40	47.36	6.8
La	0.01	45.00	6.00	41.59	2.89	6.9
Ce	0.012	80.00	5.00	73.15	7.35	10.1
Pr	0.02	8.00	n/r	9.21	0.86	9.3
Nd	0.005	39.00	5.00	35.56	2.16	6.1
Sm	0.002	7.00	1.00	6.87	0.41	6.0
Eu	0.001	1.40	0.20	1.37	0.08	6.0
Gd	0.001	5.80	n/r	5.74	0.35	6.2
Tb	0.002	0.90	0.10	0.84	0.05	6.4
Dy	0.002	4.60	n/r	4.51	0.27	6.0
Но	0.001	1.00	n/r	0.87	0.06	6.4
Er	0.001	2.60	n/r	2.51	0.16	6.5
Tm	0.001	0.42	n/r	0.36	0.03	7.5
Yb	0.001	2.90	0.40	2.38	0.15	6.5
Lu	0.001	0.40	0.05	0.35	0.03	7.5
Hf	0.001	3.90	0.70	2.44	0.19	7.7
W	0.03	4.30	n/r	3.83	0.34	8.9
Tl	0.057	n/a	n/a	0.55	0.07	12.0
Pb	0.21	21.00	3.00	20.91	1.31	6.3
Bi	0.073	n/a	n/a	0.47	0.07	14.6
Th	0.008	12.70	1.30	13.57	1.14	8.4
U	0.004	12.00	1.10	11.92	1.00	8.4

Notes. DL – the element detection limit,  $\pm$  – the certified range of measurement error,  $RSD_{abs.}$  – the absolute measurement error,  $RSD_{rel.}$  – the relative measurement error, n/a – the element not certified, n/r – the measurement error range not calculated.

Gamma-active radionuclides in the sediments of Lake Ukonlampi (Fig. 1) were measured at the Radiochemistry Department of Moscow State University using an ORTEC GEM-C5060P4-B gamma-spectrometer and ultrapure germanium (HPGe) semiconductor detector with a beryllium window (relative efficiency 20 %). The spectra were processed in the software suite SpectralineGP.

Statistical processing of the data was done in Microsoft Excel 2007. The results of the study were visualized in Inkscape 0.48.4.

### Results and discussion

This study of the collected core samples of recent sediments from small lakes in Karelia revealed an upward trend in the concentrations of chemical elements, primarily HMs, from the deeper layers of sediment to the more recent ones. This trend is most pronounced for urban lakes, mainly in the city of Petrozavodsk, which is associated both with the powerful impact of local pollution sources and with the long-range transport of pollutants (*Cnykobckuŭ*, 2018; *Medvedev et al.*, 2019). For example, in the sediment core sample from Lake Lamba located near a thermal power station in Petrozavodsk, abnormally high concentrations of V, Ni, Cr, and other metals were found in layers 0 to 20 cm deep, which is associated with the practice of burning fuel oil (*Cnykobckuŭ u ∂p.*, 2017). In addition to HMs, recent sediment layers in urban lakes demonstrate an increased concentration of lithophilic elements, e. g. lanthanides (*Cnykobckuŭ*, 2019). One of the explanations for this phenomenon may be the deposition of fine urban dust, composed of particles of silicate minerals, which are the primary concentrators of lanthanides. The dust may also originate from construction sites in the city, as well as with the practice of winter sanding of roads with a clay-sand mixture, which is easily carried by the wind in summer.

In non-urbanized areas, which can conventionally be described as reference areas, long-range transport is the main factor in the accumulation of HMs in lake sediments (*Vinogradova et al., 2017*). According to numerous studies, Pb, Cd, Hg, Tl, Sb, and Bi can be classified as the main agents of long-range transport (*Sarkar et al., 2015; Mcconnell et al., 2008; Bartnicki, 1994*). Typically, these elements are closely correlated with each other, which further supports the validity of the hypothesis about the influence of long-range transport. Most of the other elements, especially lithophilic elements, do not show pronounced abnormally high concentrations in the upper sediment layers compared to the deeper layers (*Cπυκοβεκμιμ, 2019; Slukovskii et al., 2019*). However, the study of sediment core samples from some regions of southern Karelia revealed that such elements as Zn, Cu, Sn can also exhibit the behavior typical of long-range transport agents. Considering that there are no local sources of these metals near the respective lakes, it is logical to hypothesize that these elements could also enter water bodies through atmospheric transport. In particular, this situation is observed in the lakes of the southwestern part of Karelia, which can be explained by the effects of industrial emissions from the Leningrad Region and St. Petersburg on the geochemistry of the recent sediments in Karelia (*Slukovskii et al., 2019*).

To establish the background level of chemical elements in the collected sediment core samples from the studied small lakes in the south of Karelia, two factors were taken into account: sedimentation rate in small lakes of neighboring regions (as no such data is available for Karelia) and direct analysis of the vertical distribution of marker elements in the studied sediment core samples. Pb was chosen as a marker element, because it is the most reliable indicator of historical changes in the environment 150–300 years ago (Sarkar et al., 2015; Karlsson et al., 2006; Escobar et al., 2013; Hosono et al., 2016; Dauvalter et al., 2010).

The average sedimentation rate in the small lakes of Northern Fennoscandia and Murmansk Region, which geology is similar to that of Karelia, is known to vary from 0.3 to 1.25 mm per year (Πανβαπьμερ, 2012; Rognerud et al., 2000; Håkanson, 1984). Taking into account that the southern part of Karelia has a greater share of forested areas compared to Northern Fennoscandia and Murmansk Region and that the sedimentation rate can be higher in Karelia due to the high flow rate of organic matter into the lakes, a sedimentation rate of 1.25 mm per year was adopted. Thus, sediments 30 cm thick could form over the course of approximately 240 years. However, the most pronounced changes in the accumulation of HMs in the northern environments around the world started to happen later than indicated, namely 150-170 years ago (Keinonen, 1992; Dauvalter et al., 2011; Моисеенко и др., 2000). Therefore, in the average lake, sediment layers deeper than 20 cm can be regarded as reference layers that formed in pre-industrial time. Examination of the sediment core samples from the lakes that were investigated as part of this study largely supported these assumptions. Fig. 2 shows that in all five lakes in the reference regions of southern Karelia, a noticeable increase in Pb concentrations begins at a depth of 15-25 cm. Other elements behave similarly, namely Sb, Cd, Tl, Bi, and other markers of the effects of global anthropogenic emissions on the geochemistry of the recent sediments in small lakes (Michinobu et al., 2013). This is also seen in Fig. 3, which shows that the increase in the concentrations of Pb, Cd, and Tl in the recent sediment in Lake Ukonlampi dates from the early 20th century, which is associated with the industrial development in Europe. The most noticeable increase in the concentrations of chemical elements was observed in the post-World War II period, which is associated with the active growth of the industry in the USSR. The average recent sedimentation rate in Lake Ukonlampi, according to a dating study, is 1.25 mm, which coincides with the previously adopted general value for the lakes in the south of Karelia (*Slukovskii et al., 2019*). In addition, similar sedimentation rates are observed in the southern regions of Finland and Sweden (*Karlsson et al., 2006; Verta et al., 1989*).

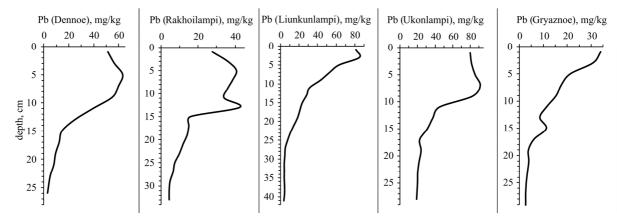


Fig. 2. Vertical distribution of Pb concentrations in the sediments core samples from small lakes in the south of Russian Karelia

Рис. 2. Вертикальное распределение концентраций Рb в образцах колонок донных отложений малых озер юга Карелии

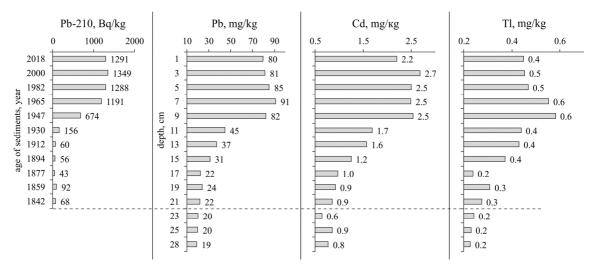


Fig. 3. The distribution of Pb-210, Pb, Cd, and Tl by depth in the sediments of Lake Ukonlampi (southwest of Karelia)

Рис. 3. Распределение Pb-210, Pb, Cd и Tl по глубине в современных отложениях озера Юконлампи (юго-запад Карелии)

However, each lake is unique, and the sedimentation rate can vary greatly even within the same region or part of the region. Therefore, to estimate the background concentrations of chemical elements in the sediments in the small lakes of Karelia, only the deepest layers of all column samples were used, where the coefficient of variation of Pb concentrations does not rise above 50-60 %. These are layers between 14 and 48 cm, depending on the particular lake. In addition, concentrations of chemical elements found in the samples collected using a hand-held drill from depths of 1 meter or deeper were included in the dataset. The age of such sediments, which formed in the interval between the deglaciation of the modern Republic of Karelia and the onset of industrialization in the countries of Europe and North America, is estimated to be thousands of years (*Cuhbkebuu u dp., 1995*). Consequently, any variations in the chemical composition of such sediments can be attributed to natural factors, which is acceptable when estimating the background concentrations of chemical elements. The resulting datasets for the 42 elements ranged from 73 to 76 samples. The concentrations of the majority of chemical elements in the samples do not follow the normal distribution, which is often the case in geochemistry; therefore, sample median values ( $x_{\rm Me}$ ), which, unlike the arithmetic mean, are less affected by any extremely high outliers in the samples, were adopted as average background concentrations. Other indicators for each of the elements are shown in Table 2.

Table 2. Background concentrations (in mg/kg) of chemical elements in the sediments of small lakes in the southern part of Russian Karelia Таблица 2. Фоновые концентрации (в мг/кг) химических элементов в отложениях малых озер южной части Карелии

Element	$x_{ m Me}$	$x_{\text{max}}$	$x_{\min}$	n
Li	2.7	23.5	0.3	76
Sc	9.0	18.6	1.9	76
Ti	286	2 174	46	76
V	32	160	2	74
Cr	18	65	6	76
Mn	437	36 610	49	76
Со	6.1	13.4	1.2	76
Ni	24.8	75.2	6.9	76
Cu	33	230	8	76
Zn	95	424	29	75
Rb	6	63	1	76
Sr	35	147	21	76
Y	7	31	2	76
Zr	32	582	4	76
Nb	0.90	6.73	0.16	76
Mo	2.0	12.4	0.5	76
Cd	0.41	1.71	0.08	73
Sn	0.56	1.77	0.34	76
Sb	0.17	0.81	0.06	76
Cs	0.35	2.03	0.03	76
Ba	250	1 461	41	76
La	12.7	50.0	2.8	76
Ce	25	116	5	76
Pr	3.0	12.8	0.6	76
Nd	11.3	49.8	2.3	76
Sm	2.21	9.98	0.58	76
Eu	0.46	1.57	0.13	76
Gd	1.69	8.35	0.50	76
Tb	0.28	1.05	0.07	76
Dy	1.46	6.25	0.37	76
Но	0.28	1.19	0.07	76
Er	0.81	3.26	0.21	76
Tm	0.11	0.42	0.03	76
Yb	0.71	2.88	0.18	76
Lu	0.10	0.42	0.03	76
Hf	0.8	12.8	0.1	76
W	0.35	2.53	0.15	76
Tl	0.14	0.52	0.05	76
Pb	4.6	21.3	0.7	76
Bi	0.08	0.70	0.03	76
Th	2.23	9.77	0.48	76
U	1.5	42.3	0.2	76

Notes.  $x_{\text{Me}}$  – the median,  $x_{\text{max}}$  and  $x_{\text{min}}$  – the maximum and minimum values of the sample, n – the number of samples.

Comparing the estimated background values for small lakes in Karelia with similar data (Даувальтер, 2012; Håkanson, 1984; Dauvalter et al., 2011; Даувальтер и др., 2014) for neighboring regions (Fig. 4), it can be seen that the values for all elements, except Cr, are almost identical in the sediments from the lakes in Karelia and Murmansk Region. Lake sediments in the Scandinavian countries show slightly elevated concentrations of Pb, Cr, Co, and Ni compared to the studied lakes in Karelia and Murmansk Region. In both cases, there is likely

a difference in the organic matter content in the sediments from the lakes of Karelia and regions located further north, since Pb, being a chalcophile element, and Cr, Co, and Ni, being siderophile elements, accumulate to a significantly greater extent in mineral deposits, which are more common in the Murmansk Region and Scandinavia. In addition, these regions may have generally increased geochemical background levels of these elements due to a large number of Pb, Cr, Co, and Ni ore occurrences and deposits.

It was also found that the background concentrations of Zn, Cr, V in the lake sediments from the south of Karelia are close to the respective values in the sediments from small lakes in southern Norway (*Rognerud et al., 2000*). On the other hand, the Norwegian sediments have a slightly higher enrichment factor of Co, Pb, and Mn, compared to the Karelian lakes, which we attribute to the multiple ore occurrences of the respective elements in southern Norway and a slightly lower enrichment factor of Cu, Ni, and Cd, compared to the Karelian lakes. The latter may also be associated with the geochemical features of each of the regions. For example, elevated Cu concentrations in the surface waters in the southern part of Karelia and increased background levels of Cd in the rivers of Karelia were previously noted (Белкина и др., 2012).

# ☐ Republic of Karelia ☐ Murmansk region ☐ Scandinavian countries

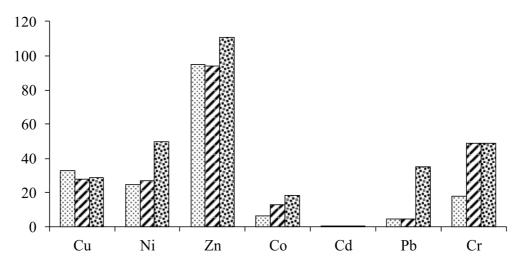


Fig. 4. Average background levels of heavy metals in the sediments of the lakes in the south of Karelia, Murmansk Region, and Scandinavian countries Рис. 4. Средние фоновые уровни содержания тяжелых металлов в донных отложениях озер юга Карелии, Мурманской области и стран Скандинавии

The averaged concentrations of rare-earth elements (REE) in the sediments of lakes in the south of Karelia have a similar distribution pattern with the trend for the upper continental crust (Fig. 5), whose composition is usually adopted to analyze the behavior of lithophilic elements (*Humepnpemaqua*..., 2001; Sun et al., 1989; Wedepohl, 1995). In both cases, enrichment in light REEs and a negative Eu anomaly are typical. However, at the same time, the total REE content in the upper continental crust is much higher than in the sediments of Karelian lakes, which is due to the fact that in sediments with a high organic matter content, which also applies to the studied lake sediments, the total REE content tends to be low. The accumulation of these elements is usually controlled by the terrigenous fraction of the sediment, therefore the total REE content is usually higher in the mineral sediment, where the organic fraction does not exceed 10–15 % (*Cmpaxobehko*, 2011). In addition to REE, whose levels are low – compared to the average continental crust – in the background layers of the sediments of small lakes in the south of Karelia, the levels of other chemical elements, except Mo, are also low. Mo ores and ore occurrences are common in Karelia (*Muhepanho-chipheban*..., 2006), which probably contributed to its accumulation in pre-industrial times. On the other hand, the upper sediment layers of the studied lakes are significantly enriched in elements such as Pb, Cd, Tl, Zn, Cu, W, V compared with the average continental crust, which is explained by the anthropogenic factor (*Cnykobckuŭ*, 2018).

A comparative analysis of the concentrations of various chemical elements in the lake sediments collected for this study and in the river sediments collected in Karelia's reference areas ( $\Gamma$ eoxumuveckoe..., 2004) showed a fairly close level of accumulation within the same region (Fig. 6). A minor difference is noted only for Cu, Ba, and Zn, which are better represented in lake sediment with a high content of organic matter, and for Li, Cr, and Sr, which accumulate more intensively in stream and river sediments due to the abundance of the terrigenous fraction, which predominantly contains lithophile elements. But in general, the data collected for lake sediments

in the south of Karelia is comparable with similar data for stream sediments, as well as for lake sediments in the neighboring regions of Russia and other countries.

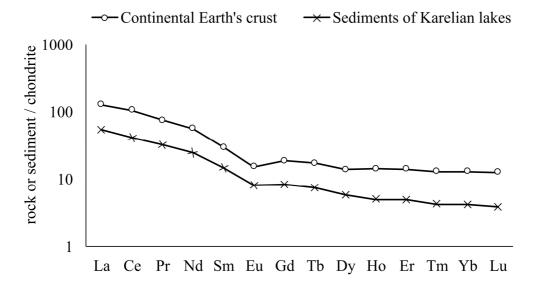


Fig. 5. Trends of chondrite normalized (*Белкина и др., 2012*) averaged REE levels in the lakes in the south of Karelia compared to the continental crust Puc. 5. Тренды нормализованных по хондриту (*Белкина и др., 2012*) усредненных содержаний РЗЭ в озерах юга Карелии по сравнению с континентальной корой

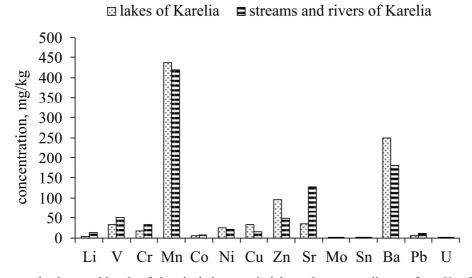


Fig. 6. Average background levels of chemical elements in lake and stream sediments from Karelia's south Puc. 6. Средние фоновые уровни химических элементов в озерных и речных отложениях юга Карелии

On the other hand, one cannot but take into account the fact that contemporary studies and those conducted earlier employ completely different methods and instruments and may have purely technical inconsistencies that are not related to the natural distribution patterns of chemical elements. Ultimately, the results will be most relevant when studying lake sediments in the northern regions of Russia, geologically close to the southern part of Karelia. In addition, further studies will be conducted to collect more accurate data on the background levels of chemical elements in heterogeneous lake sediments in the Republic of Karelia and, possibly, neighboring regions. Large-scale similar studies in Siberia have shown that organic silts, mineral, ferruginous, and carbonate sediments can have significant differences in terms of geochemistry (*Cmpaxobehko*, 2011). Considering that in Karelia and Murmansk Region, in addition to carbonate sediments, almost all types of recent lake sediment are present, which also include diatomites and diatom sapropels containing a significant share of fossil diatom valves (*Cuhbkebuy u др.*, 1995; Демидов и др., 2006), such studies appear to be highly relevant. Moreover, one should take into account the absence in Russia of any standards governing the concentrations of chemical elements, primarily HMs, in the sediments of different water bodies.

### **Conclusion**

As a result of this study of 15 small lakes in the southern part of the Republic of Karelia and core samples of the sediments from these lakes, the average content of 42 chemical elements, including heavy metals, was estimated, which can be used as background values for the study area. Our analysis of the obtained background values showed that the deeper (pre-industrial) sediment layers in the lakes are significantly depleted in all elements compared to the continental crust. An exception is Mo, whose ores and ore occurrences are widespread in the south of Karelia. In addition, it was found that the averaged concentrations of rare-earth elements in the sediments of lakes in the south of Karelia have a similar distribution pattern with the trend observed in the upper continental crust. Enrichment in light rare-earth elements and a negative Eu anomaly were observed. A comparative analysis of the obtained background levels of Pb, Cd, Cu, Ni, Zn, Cr and similar data from the Murmansk Region and Scandinavian countries highlighted the compared values that are similar. In addition, similar values were obtained when comparing the average concentrations of chemical elements in the lake and river and stream sediments in the south of Karelia. A minor difference was found only for Sr, V, and Cr that to a large extent gravitate toward the terrigenous fraction of the sediments, which is better represented in stream sediments. Our findings can form the basis for an extensive study of the background concentrations of chemical elements in sediments throughout the Republic of Karelia, including the identification of the background values of elements for different lithological types of sediment (sapropels, diatomites, mineral, ferruginous, and carbonate sediments).

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