The spatio-temporal distribution of elements in the bottom sediments of Lake Onego and small lakes located on the catchment area of Onego Ice Lake*

V. D. Strakhovenko[1,2], N. A. Belkina[3,4], N. A. Efremenko[3], M. S. Potakhin[3,4,5], D. A. Subetto[4], V. I. Malov[1,2], E. A. Ovdina[1]

[1] Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences, 3, pr. Akademika Koptyuga, Novosibirsk, 630090, Russian Federation
[2] Novosibirsk State University, 2, ul. Pirogova, Novosibirsk, 630090, Russian Federation
[3] Northern Water Problems Institute of the Karelian Research Centre of the Russian Academy of Sciences, 50, pr. Aleksandra Nevskogo, Petrozavodsk, 185030, Russian Federation
[4] Herzen State Pedagogical University of Russia, 48, nab. r. Moyki, St. Petersburg, 191186, Russian Federation
[5] Petrozavodsk State University, 33, ul. Lenina, Petrozavodsk, 185910, Russian Federation

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The work presents the results of a comprehensive mineralogical and geochemical study of Late Pleistocene-Holocene bottom sediments of Lake Onego and small lakes located in the territory belonging to Onego Ice Lake. Methods of ICP-MS, atomic absorption spectrometry, X-ray fluorescence analysis, X-ray phase method (XRD), scanning electron microscopy (SEM), and gamma-spectrometric method were used. The geochemical composition of the terrigenous fraction reflects the mineral composition and is permanent for the all bottom sediments cores of Lake Onego and small lakes during time interval about 12.000 years. For the first time, detailed mineralogical studies of sediments have shown that the composition of mineral associations of the terrigenous fraction is similar in the bottom sediment cores of Lake Onego and small lakes. The association of authigenic minerals in bottom sediments is distinguished by the presence of pyrite framboids in small lakes, and crystalline aggregates of Fe-phosphate, ferruginous illites and chlorites in Lake Onego. Sedimentation rates established by the study of correlations the indicator technogenic radioisotope ^{137}Cs and atmospheric ^{210}Pb. In the bottom sediments of small lakes, sedimentation rates vary from lake to lake, as well as in various areas of Lake Onego in the range from 0.05 cm/year to 0.30 cm/year.

Keywords: Lake Onego, small lakes, Onego Ice Lake, bottom sediments, mineralogy, geochemistry, sedimentation rate, ^{210}Pb, ^{137}Cs.

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1. Introduction

Lake Onego is a unique reservoir located among the crystalline rocks of the Baltic Shield and the Vendian-Phanerozoic sedimentary rocks of the Russian Platform. The lake basin has tectonic origin and has been altered by Pleistocene glaciers (Biske et al., 1971; Palaeoproterozoic Onega…, 2011). According to the scheme of the geological structure of the Karelian Massif and its framing, the catchment area of Lake Onego is composed mainly of gneiss-granites of the base complex (aged about 3 billion years) and Paleoproterozoic volcanogenic-sedimentary complexes. In the south and southeast, deposits of the Riphean-Phanerozoic cover of the Russian Platform are common (Palaeoproterozoic Onega…, 2011). The Late Weichselian Scandinavian Ice Sheet and the development of a vast meltwater reservoir (Onego Ice Lake (OIL)) have made changes associated with the degradation of sedimentary rocks (Subetto et al., 2016; Hang et al., 2019).

The catchment area of Lake Onego belongs to the subdistrict of iron-silica-humus accumulation, where surface waters are significantly enriched with Fe and Si (Kholodov et al., 2012). The formation time of the Lake Onego basin in the Onego depression is about 13,000 years ago (Biske et al., 1971; Saarnisto and Saarinen, 2001; Demidov, 2005; Subetto et al., 2019). In recent years, the study of the Lake Onego bottom sediments has been carried out within the framework of limnological studies. The purpose of which was to characterize in detail the various stages of Lake Onego development (Saarnisto and Saarinen, 2001; Hang et al., 2019; Subetto et al., 2019; Zobkov et al., 2019) and evaluate the condition of the ecosystem under anthropogenic influence (Subetto et al., 2016; Belkina and Kulik, 2019).

One of the main sources of substances entering lake systems is atmospheric dust and aerosols (Kholodov et al., 2012; Shevchenko et al., 2017). In the process of atmospheric transport over long distances, fine dusty particles and aerosols are enriched with heavy metals (Cd, Hg, Sb, etc.) selectively (Grebenshchikova et al., 2008). The atmospheric component is especially high for biogenic elements (P, N, and C) that determine the development of living organisms (Kabata-Pendias, 2001). A large amount of factual material has shown that the interaction of production and destruction of organic matter ultimately determines, along with other factors, the characteristics of small lakes bottom sediments (Bernier-Latmani et al., 2010; Strakhovenko et al., 2021a).

Since the beginning of nuclear weapons testing long-lived isotopes (^{90}Sr, etc.), settling on microparticles, are involved in the biogeochemical cycle (Izrael, 1996). Against the background of the existing latitudinal zoning in the distribution of the ^{137}Cs global background, there is a mosaic distribution of radiocesium for local and regional atmospheric precipitation (Izrael, 1996; Rikhvanov, 2009).

The aim of the work is to assess the role of microparticles in the capture and accumulation of artificial radionuclides and pollutants (Hg, Cd, Pb, etc.) in the bottom sediments of Lake Onego, their evolution during the Holocene in order to establish their sources.

Based on the study of correlations of the multi-element composition of natural stratified bottom sediments of individual sections of the lake, in comparison with the indicator technogenic radioisotope ^{137}Cs, atmospheric ^{210}Pb, elements associated with various sources of intake will be identified and the contribution of the participation of microparticles in their transfer and formation of bottom sediments will be assessed. The Lake Onego bottom sediments were compared with the bottom sediments of small lakes to assess the sources of sedimentary matter of natural and anthropogenic nature based on lithostratigraphic, geochemical and mineralogical data. Small lakes (located in the territory belonging to OIL) separated from Lake Onego at different times of the Holocene.

2. Study area

The sampling, mineralogical, and geochemical studies of bottom sediment cores were carried out from different areas of Lake Onego and small lakes (Fig. 1). The catchment area of the studied small lakes is characterized by the common climatic conditions of the entire catchment basin, as well as the heterogeneity of the geological and geomorphological structure. Numerous small lakes of Karelia, formed due to the deglaciation of the Last Valdai glaciation as elements of the landscape, in the course of their existence passed a number of development stages. These stages are from accumulators of mineral terrigenous material during the Pleistocene (nival conditions) to the development of Holocene aquatic ecosystems producing organic matter (humid conditions) (Kuznetsov and Subetto, 2019).

The small lakes basins in general are located among the rocks of the Baltic Shield. The Rovskoye and Velikoye Lakes are located on sedimentary rocks of the Russian Plate and according to the genesis of the lake belong to the residual basins, and are a relic of the OIL. The waters of the small lakes correspond to the mesohumus bicarbonate medium-alkaline, slightly acidic, and neutral type of the calcium and magnesium group.

In all the studied small lakes, there is a two-stage structure of bottom sediment cores: The OIL stage (varved clays) and organic-mineral silts stage. They are isolated with a gradual increase of matter to the water-bottom sediment boundary. The uppermost part of the bottom sediment sections is composed of sapropel, which is a colloidal soft fatty mass of brown, sometimes almost black or olive color, containing 70–90 % water and at least 50 % organic matter. A clear lithological boundary, visually expressed in the color change of bottom sediments from gray to dark brown or greenish-brown, is associated with a sharp increase of the organic matter content. This lithological boundary in the lacustrine sediments in the eastern part of Europe records the Younger Dryas/Preboreal/Boreal transitional time interval (10,300–9,000 ^{14}C years ago) (Subetto, 2009).

Earlier studies described in detail the various stages of the Lake Onego development (Saarnisto and Saarinen, 2001; Hang et al., 2019, Subetto et al., 2019; Zobkov et al., 2019; Strakhovenko et al., 2021b). The initial stage of lake formation is associated with the formation of the OIL about 14.5 thousand years ago. About 13.3 thousand years ago, typical varved clays were deposited at the bottom of the OIL. At the end of the Allerod — the beginning of the Late Dryas, during the regression, the OIL area decreased by almost one and a half times. According to radiocarbon dating, the isolation of the studied small lakes from Lake Onego occurred at different times of the Holocene (more than 8 thousand years ago) (Hang et al., 2019; Subetto et al., 2019; Zobkov et al., 2019).

3. Material and Methods

In the period from 2018 to 2021, drilling was carried out from the ice of Unitskaya and Petrozavodsk Bays and small lakes located on the territory belonging to OIL. The sampling of short cores of bottom sediments was carried out by a stratometer “Limnos” and long cores — by a modified peat drill. The fieldwork on Lake Onego was carried out

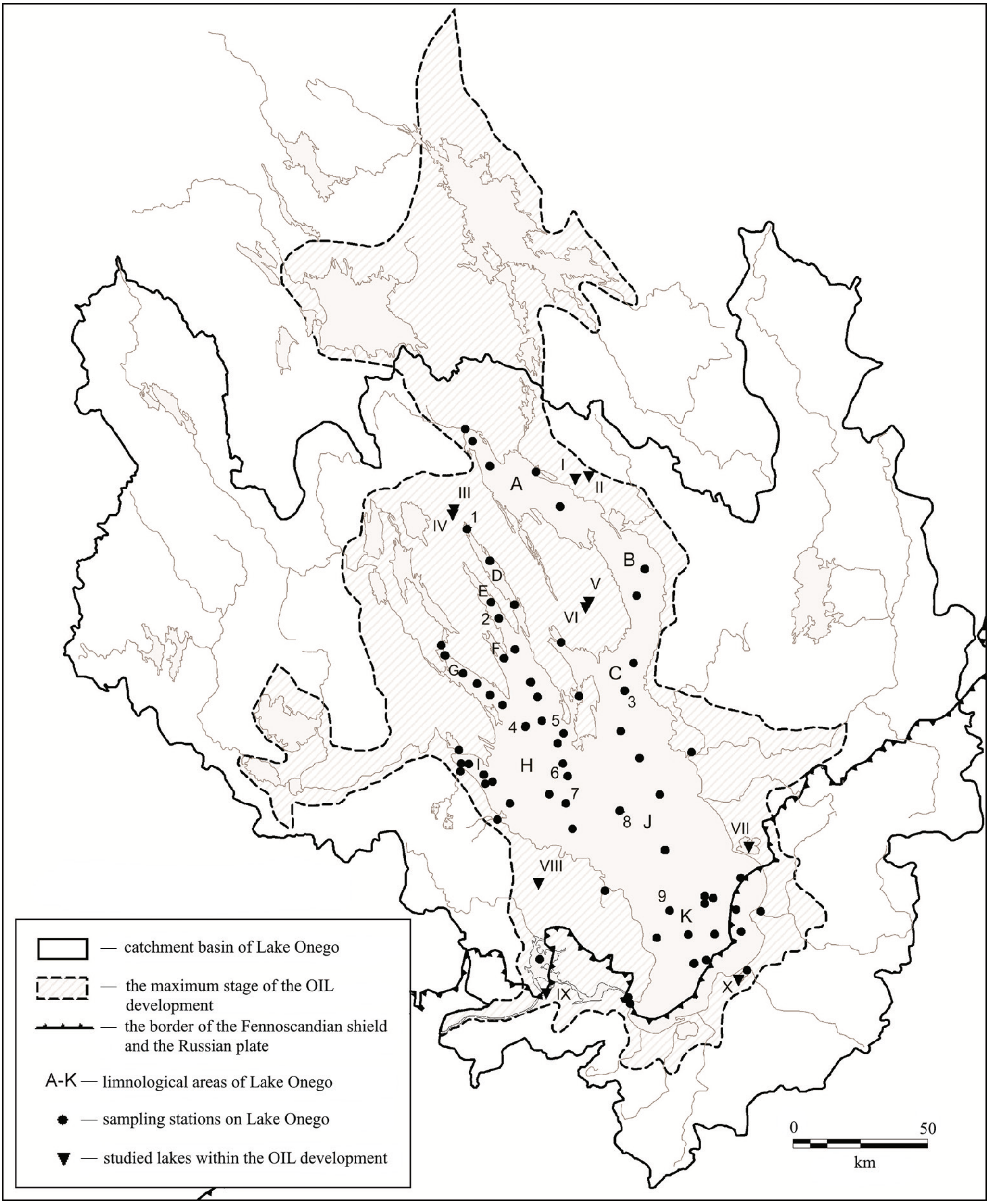


Fig. 1. Limnological areas and the catchment area of Lake Onego with sampling points of sediment cores in the areas of Onego Ice Lake and small lakes. Limnological areas: Povenetsky Bay (A), Zaonezhsky Bay (B), Small Onego (C), Unitskaya Bay (D), Lizhemskaya Bay (E), Gorskaya Bay (F), Kondopoga Bay (G), Big Onego (H), Petrozavodsk Bay (I), Central Onego (J), South Onego (K). The studied small lakes:

I — Bezymyannoe; II — Munozero; III — Lavkozero; IV — Gangozero; V — Keratskoye; VI — Polevskoye; VII — Muromskoye; VIII — Rzhanoe; IX — Rovskoye; X — Velikoe. Sampling stations where the sedimentation rate was calculated: 1 — Un; 2 — GL3; 3 — L18; 4 — R03; 5 — Be; 6 — C2; 7 — R01; 8 — C01; 9 — S06 in 2016–2021. Sixteen cores of bottom sediments up to 3 m long were sampled from the board of Research vessel "Ecolog" using a gravity tube (length 3 m, diameter 127 mm). The Limnos and Perfiliev stratometers and the GOIN tube were used to sample the upper undisturbed Holocene lacustrine sediments with layer-by-layer sampling (1–2 cm).

Geochemical and mineralogical study of bottom sediments was carried out at the Analytical Center for multi-elemental and isotope research SB RAS (Novosibirsk): Oxidized silts (27 samples), homogeneous silts (178 samples) and varved clays (56 samples) from 18 bottom sediments cores from different areas of Lake Onego and small lakes (homogeneous silts (97 samples), varved clays (41 samples)). Methods of ICP-MS for 32 elements, atomic absorption spectrometry for 28 elements, X-ray fluorescence analysis for 12 components, X-ray phase method (XRD), and scanning electron microscopy (SEM) were used. Gamma-spectrometric method on a planar semiconductor detector with protection from natural radiation based on especially pure lead and wolfram was used for radioisotopes to estimate the rates of modern sedimentation by the activity of ^{137}Cs and ^{210}Pb (McCall et al., 1984; Gavshin et al., 1999). Under conditions of calm sedimentation, the activity of "atmospheric" ^{210}Pb decreases exponentially from the maximum near the sediment surface, in accordance with the law of radioactive decay (Melgunov et al., 2003). By comparing the distribution of ^{210}Pb with ^{137}Cs (which records the dates of the beginning and the end of nuclear weapons tests in the atmosphere) in the sediments, additional reference time horizons can be determined (McCall et al., 1984). The authors use the CRS (the Constant Rate of Supply) model also known as the Constant Flux model (CF) (McCall et al., 1984). With the accumulation of experimental data on the dating of bottom sediments by the nonequilibrium ^{210}Pb method, it turned out that the requirement for a constant rate of sediment accumulation is often impossible. Therefore, when processing the results, the integral activity of excess ^{210}Pb is calculated below the horizon for which the age is determined. At the same time, certain assumptions must be observed: The flow of ^{210}Pb into sediments is constant; the sedimentation rate within the period under consideration (a small part of the core (1 sample) does not change; there is no post-sedimentation migration of ^{210}Pb (Gavshin et al., 1999).

4. Results

A detailed description of the geochemical and mineral composition of the Lake Onego bottom sediments, obtained using modern analytical methods, is given in the works of Strakhovenko V. D. with co-authors (Strakhovenko et al., 2020a; Strakhovenko et al., 2020b; Strakhovenko et al., 2021b; Strakhovenko et al., 2022). These studies show that the Upper Holocene bottom sediments of Lake Onego as a whole inherit the composition of terrigenous material entering the reservoir with river runoff. The presence of two types of stratification of Upper Holocene bottom sediments in different areas of Lake Onego is determined by the amount of oxygen in the near-bottom waters and the location of the lake in the northern humid zone (Fig. 2). The location of Lake Onego in the iron-manganese geochemical province determines the formation of ore layers with a high content of oxygen in the near-bottom waters at a certain depth from the water‑bottom sediment boundary. In conditions of oxygen deficiency, a low-thick fluffy layer is formed at the water-bottom sediment boundary (up to 3 cm). Gray-green homogeneous silts lie below the fluffy layer, similar to those present below the oxidized layer in cores of the first

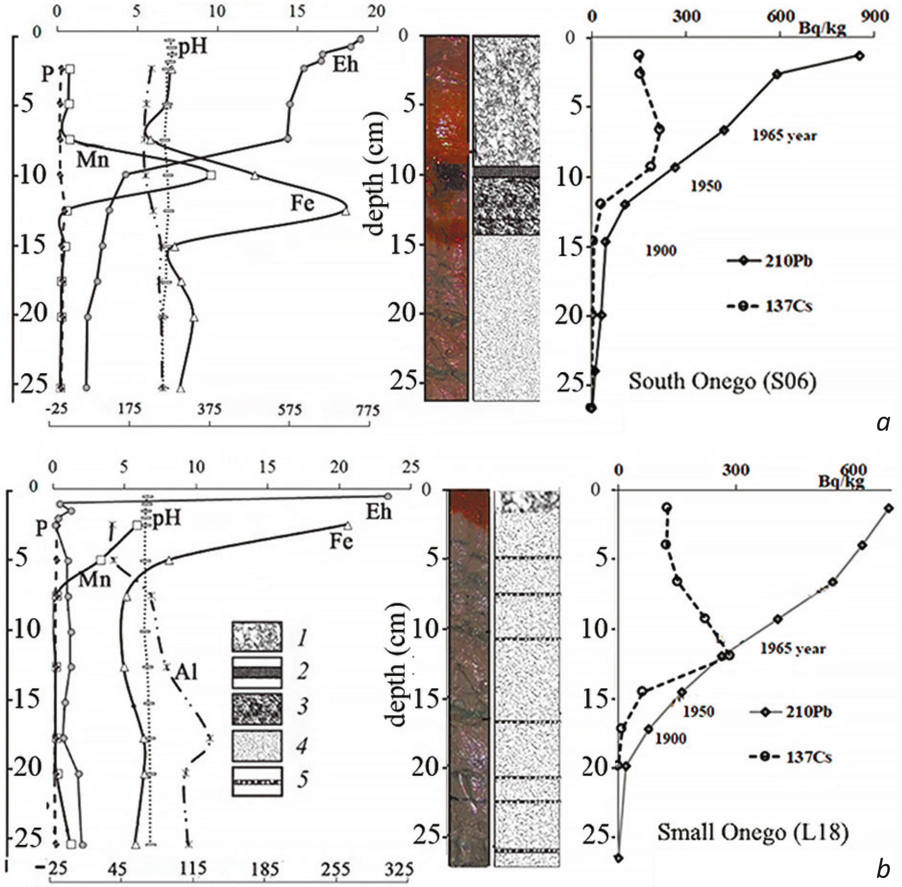


Fig. 2. Stratigraphic section of two types of sediment cores of Lake Onego (*a* — 1st type; *b* — 2nd type), vertical distribution of concentrations of Fe, Mn, Al, P (mass. %), pH (number; upper abscissa axis), Eh (mV; lower abscissa axis) distribution of Fe, Mn, Al, P (mass %), pH (on the upper X axis), Eh (mV, in the lower part of the X axis) and vertical distribution of ^{137}Cs specific activity (Bq/kg), ^{210}Pb (Bq/kg) in the bottom sediments cores of the (*a*) 1st type (South Onego, S06) and (*b*) the 2nd type (Small Onego, L18):

1 — pelitic sludge of the oxidized zone; 2 — upper black ore crust layer (mineral phases Mn); 3 — lower chocolate-colored ore crust layer (mineral phase Fe); 4 — homogeneous grayish-green silt; 5 — black, gray and green microlayers in homogeneous silt (vivianite, rhodochrosite, siderite, pyrolusite)

type. Further, down the section, a layer of aleuropelite gradually compacting Holocene silts of grayish-green color is underlain by homogeneous clays, which are replaced by varved clays below. In the present work, a detailed study of the distribution of major and trace elements of bottom sediments of Lake Onego and small lakes located in the territory belonging to Onego Ice Lake has been carried out.

4.1. Sedimentation rates to different types of stratification

A detailed study of the distribution of ^{210}Pb (through 1 cm) and ^{137}Cs was carried out in the cores of bottom sediments from different areas of Lake Onego belonging to different types of stratification (Fig. 2). The distribution of ^{137}Cs in bottom sediments is characterized by the presence of a distinct peak of ^{137}Cs activity at different depths in the bottom sediments cores in different parts of Lake Onego, and the specific activity of the radioisotope is decreased up and down the section. The growth of ^{137}Cs activity in vertical sections of the Lake Onego sediments begins from a depth of 11–15 cm (Small and Big Onego) and 7–9 cm (Central, South Onego and bays) and increases up the section to a depth of 7–9 cm (Small and Big Onego) and 4 cm (Central, South Onego and bays). According to calculations based on the distribution of ^{210}Pb, this depth in both cases correlates with 1950–1955, i. e. with the beginning of nuclear tests.

It is important to note that the distribution graphs of ^{210}Pb and ^{137}Cs in 1st and 2nd core types are the same and, therefore, the distribution of ^{210}Pb and ^{137}Cs is not affected by the type of diagenesis (Figs 2, 3). The sedimentation rates in the different areas of Lake Onego are in Big Onego, Small Onego, Lizhemskaya Bay — 0.12–0.15 cm/year; South Onego — 0.10 cm/year; Central Onego, Unitskaya Bay — about 0.05 cm/year.

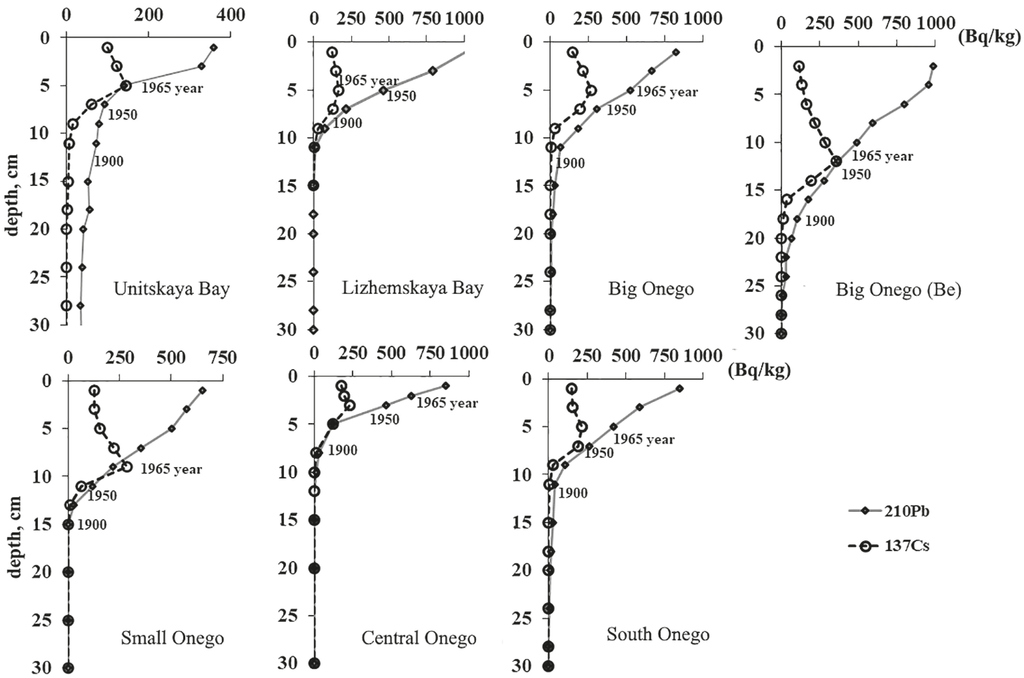


Fig. 3. Vertical distribution of specific activity of ^{137}Cs (Bq/kg) and ^{210}Pb in bottom sediments of different areas of Lake Onego

In small lakes, the rates of undisturbed sedimentation vary greatly from lake to lake according to the calculations of sedimentation rates (the CRS model) and compared with the distribution graphs of ^{137}Cs. The minimum sedimentation rate among the studied

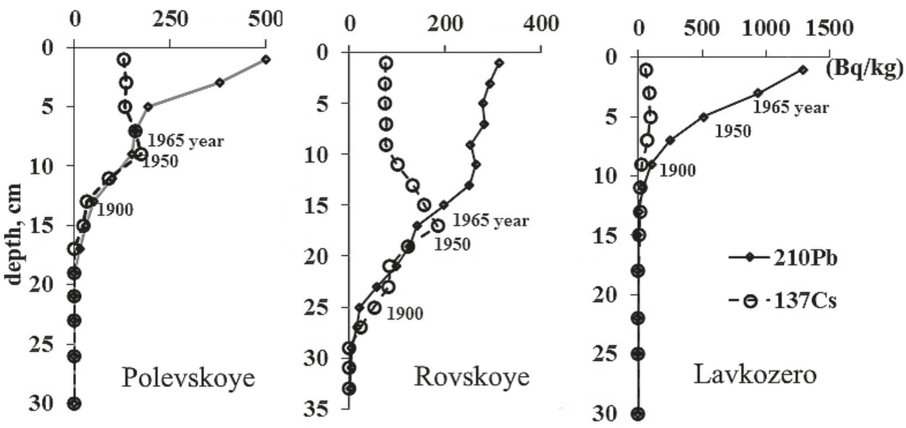


Fig. 4. Vertical distribution of the specific activity of ^{137}Cs (Bq/kg) and ^{210}Pb in the bottom sediments of small lakes located in the territory belonging to the OIL

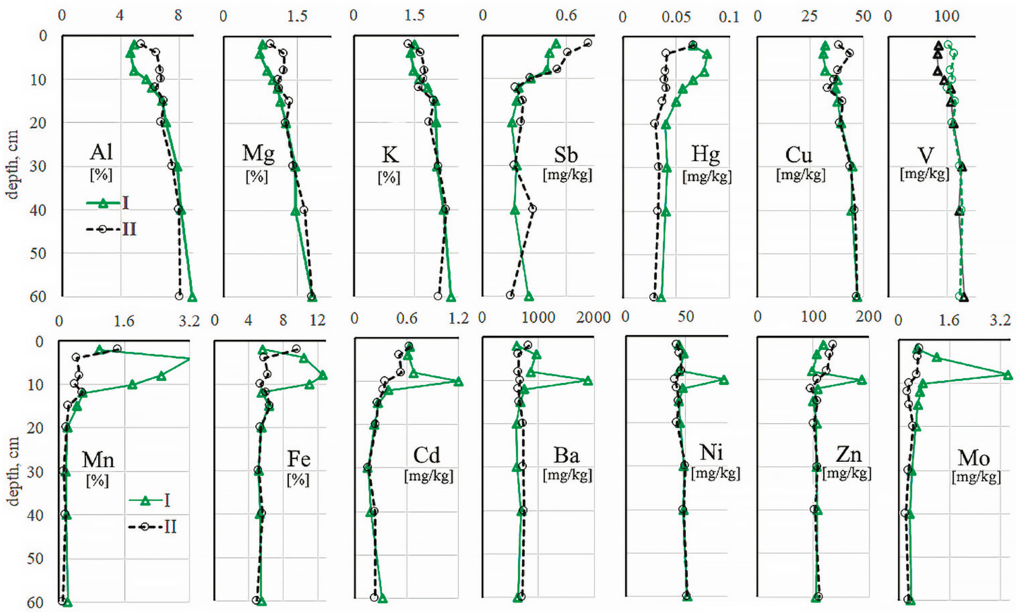
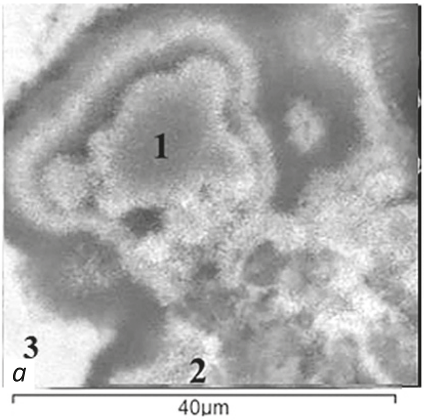


Fig. 5. Vertical distribution of elements in cores of two types of stratification of bottom sediments from Lake Onego (triangle — type 1, circle — type 2)

lakes was noted in Lake Lavkozero (0.06 cm/year), and the maximum in Lake Rovskoye (0.30 cm/year) (Fig. 4). According to calculations, the sedimentation rate in small lakes is about 0.12–0.15 cm/year (for example, Lake Polevskoe).

A comparative analysis of the vertical distribution of major and trace elements in the upper part of cores of the 1st and 2nd stratification type of the Lake Onego bottom sediments allows us to divide the studied elements into two groups (Fig. 5). The first group of elements is formed by Fe and Mn, which form ore layers, and Ba, P, Cd, Ni, Zn, Mo, Ce



%	1	2	3
Mn	44.2	39.5	1.2
Fe	----	1.5	59.4
Ca	1.2	2.6	----
Ba	----	4.5	----
Ni	----	0.8	----
Zn	----	0.6	----
Mo	----	0.3	1.1

---- the number of the element is less than 0.1 %

b

Fig. 6. Photos made using SEM of manganese-ferruginous globular formations (*a*) and a table of the composition of their zones (*b*):

in the photo and table: 1 — zones of Mn oxides; 2 — zone of Mn oxides with different degrees of crystallinity and the amount of impurities; 3 — zone of Fe hydroxides

are added to them. These elements in the zone of Fe-Mn microconcretions formation have peak contents. This distribution can be explained by the sorption processes of this group of elements by Fe-Mn mineral phases, which is well confirmed by SEM studies (Fig. 6). For the rest of the studied elements, a comparison of the vertical distribution in stratified cores of 1st and 2nd type showed that it does not differ significantly. Similar conditions of free O_2 deficiency for Lake Onego 2nd type core are realized during the bottom sediments formation of small lakes due to the mineralization of a significant amount of organic matter at the water-bottom sediment boundary. In the comparative analysis of the elements' distribution in the upper part of the cores of the Lake Onego bottom sediments with the bottom sediments of small lakes, analytical data were used only for 2nd core type. In 2nd core type, under conditions of free O_2 deficiency, when the redox boundary is located in the fluffy layer, the migration of soluble Mn^{2+}, Fe^{2+}, P and some other elements with variable valence occurs from the lower layers of sediments to the water-bottom sediment boundary (Strakhovenko et al., 2020b).

4.2. Lateral distribution of major and trace elements

Analytical data on the major and trace elements of bottom sediments for different areas of Lake Onego and small lakes are grouped and averaged over three main lithostratigraphic horizons for Lake Onego (varved clays, homogeneous silts, oxidized silts) and two for small lakes (varved clays, homogeneous silts) (Supplementary 1[1]). To compare the analytical data obtained, it shows the average values of elements for rocks composing the catchment area of Lake Onego and small lakes by (Ronov and Migdisov, 1996; Filippov, 2002; Romashkin et al., 2014).

[1] Supplementary 1 hereinafter is available at the following link: https://escjournal.spbu.ru/article/view/14223/11252 [Accessed 24.05.2022].

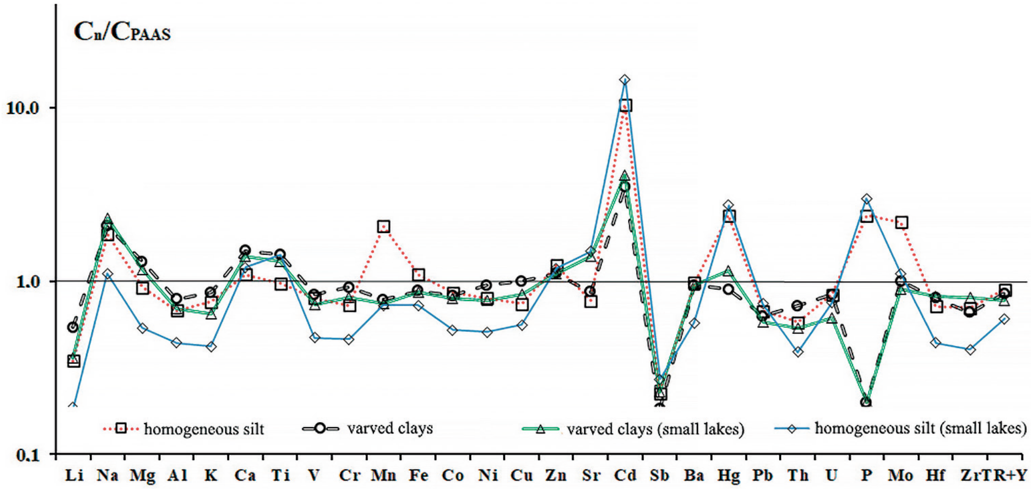


Fig. 7. Spectra of element contents in varved clays and homogeneous silts of bottom sediments cores of Lake Onego and small lakes, normalized by PAAS (Taylor and McLennan, 1985)

For almost all the studied elements, the weighted average values of the contents in the same type of lithostratigraphical horizon of bottom sediments from different areas of Lake Onego are close to the average composition of rocks in the catchment area. The variation in the contents of the studied elements does not exceed the arithmetic mean $\pm 2\sigma$ (two standard deviations), except for Mn in homogeneous silts. After comparing the concentrations of elements in samples of bottom sediments from different areas of Lake Onego and small lakes, it can be argued that the average contents in varved clays either are the same or differ within one standard deviation. In homogeneous silts, the difference for a number of elements exceeds two and sometimes three standard deviations. In homogeneous silts of small lakes, the absolute contents of Cd, Sb, Hg are significantly higher and Al, Fe, Mn, Ti, Th, Cu, Zn, U are lower (Supplementary 1, Fig. 7). It is important to note that the absolute contents for the remaining studied elements in the bottom sediments of small lakes varies within the values for the bottom sediments of different areas of Lake Onego, i. e. within the values for the rocks of the catchment area. The contents obtained by us for almost all the studied elements have the same order of values as in the bottom silts of the White Sea and other seas of the Arctic region (Shevchenko, 2006; The White Sea system…, 2017).

4.3. Comparison of the mineral composition in the bottom sediments of Lake Onego and small lakes

Comparison of the mineral composition in the bottom sediments of Lake Onego with the mineral composition of the bottom silts of small lakes was carried out using X-ray diffractometry (XRD) as well as a detailed study of textural and structural features of sediments, morphological features of minerals, chemical composition and structural data at the level of individual grains, accretions and pseudomorphoses with using SEM. The main components of homogeneous silts of small lakes are minerals of the terrigenous fraction of the pelitic dimension, numerous diatoms and macrophyte

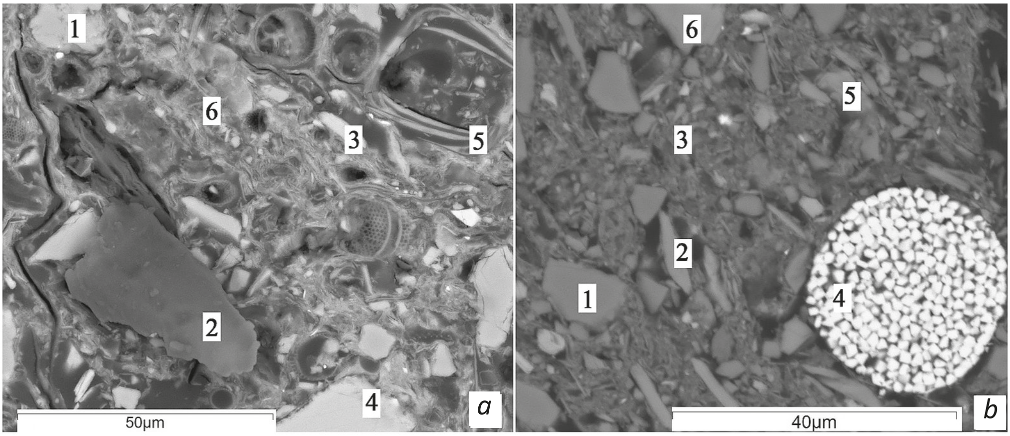


Fig. 8. Micrographs made using SEM. The mineral composition of the bottom sediments of small lakes, sampled in Lakes Velikoe (*a*) and Lavkozero (*b*). Individual grains, crystals of minerals, their aggregates and mortmass:

a: 1 — andesine, 2 — macrophyte mortmass, 3 — muscovite, 4 — potassium feldspar, 5 — skeletons and fragments of diatom shells, 6 — illite (Fe : Mg = 3 : 1); *b*: 1 — quartz, 2 — muscovite, 3 — chlorite (Fe : Mg = 2 : 1), 4 — pyrite framboids, 5 — albite, 6 — potassium feldspar

mortmass. Among the terrigenous minerals of different morphology and degree of rolling in bottom sediments, there are individual grains of quartz and feldspar (microcline, albite and andesine), muscovite and chlorite (Fe : Mg = 2 : 1). In a subordinate amount, there are grains of epidote, titanite, actinolite, diopside, hornblende and accessory minerals (magnetite, rutile, ilmenite, zircon, hematite, pyrite, etc.). Larger individual grains of these minerals are found in the tangled fibrous mass of illite (Fe : Mg = 3 : 1) (Fig. 8).

The presence of pyrite framboids in the samples from the first centimeters of the bottom sediments of all the studied small lakes indicates the reducing conditions of sedimentation. The main difference in the mineral composition of the small lakes bottom sediments is manifested in the composition of fine-scaled, tangled fibrous aggregates of illite and chlorite. In the bottom silts of Lake Onego, these aggregates are represented exclusively by Fe-illites and Fe-chlorites, in which magnesium is practically absent. In the bottom sediments of small lakes in tangled fibrous aggregates of illite and chlorite, the ratio Fe : Mg fluctuates about 3:1 (Fig. 9). This difference may be due to the time spent by the illites in the water mass. In the conditions of the northern climate, aggregates of illite and chlorite are entered by rivers into lakes in a degraded state (Fedorets, 2009). In (Rateev et al., 2008; Lisitsyn, 2014) it is shown that illites and chlorites do not change during transfer, but undergo significant transformation only in the final reservoir of the runoff.

The entered degraded aggregates of illite and chlorite are present in the Lake Onego waters for a considerable time. And Fe, which is present in lake water in significant quantities, can be adsorbed by degraded aggregates of these minerals, which are regenerated to normal Fe-illites and chlorites directly in lake water or during the initial stage of diagenesis in the uppermost layers of sediments. Fe-illite and Fe-chlorite can also be the result of the transformation of mineral suspension during various processes involving living matter directly in the bottom layer. Since small lakes are mostly shallow, degraded aggregates of illites and chlorites quickly reach the bottom and do not have time to adsorb

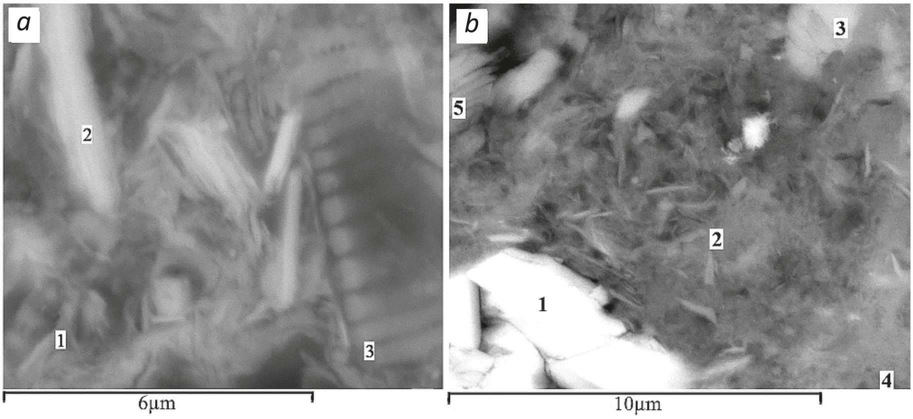


Fig. 9. Micrographs made using SEM, the mineral composition of the bottom sediments of small lakes, (*a*) sampled in Lake Munozero and (*b*) bottom sediments of Lake Onego (Central Onego). Individual grains, crystals of minerals, their aggregates, skeletons and fragments of diatom shells:

a: 1 — an aggregate of tangled fibrous illite (Fe : Mg = 3 : 1), 2 — weakly cleaved muscovite, 3 — skeletons and fragments of diatom shells; *b*: 1 — epidote crystal, 2 — aggregate of tangled fibrous illite (Fe : Mg = 2 : 1), 3 — weakly deformed potassium feldspar aggregate, 4 — skeletons and fragments of diatom shells, 5 — coarse-scaled chlorite aggregate (Fe : Mg = 3 : 1)

iron from the water. Further, under conditions of reducing diagenesis, up to illites and chlorites are regenerated, which contain both iron and magnesium (Fe : Mg = 2 : 1 or 3 : 1).

4.4. Vertical distribution of major and trace elements of Lake Onego and small lakes

The vertical distribution of elements in stratified generalized bottom sediments cores of Lake Onego and small lakes from varved clays to modern sediments is compared (Fig. 10, Supplementary 1). The graphs analysis of the elements distribution by shape, slope, and features of the spectra variability, taking into account the mineral composition of the bottom sediments cores from different areas of Lake Onego and small lakes, allows us to divide the studied elements into three groups.

In the first group of elements, the vertical spectra are of the same configuration with each other across the entire water area of Lake Onego and small lakes. The vertical curves have a slight slope towards increasing concentrations with depth and reach maximum values in varved clays (Na, Al, Mg, K, Rb, Zr, Th, Be, Li, Nb, V, Sr, Co, Cr, Ta, Cs, Hf, TR (except Eu, Ce)). It is important to note that the absolute values of the concentrations of these elements may vary greatly.

The second group includes elements characterized by either a gradual decrease in the contents in sections down and for some elements by more than 2 times (Mn, Cd, Hg, Pb, Sb), or the presence of peak contents at the redox boundary. The distribution of elements either coincides with the general slope of the spectrum in the 1st and 2nd types of sediment cores in Lake Onego, differing from small lakes, or differs in the cores of Lake Onego, coinciding with the cores in small lakes. The formation of ore layers leads to peak concentrations of Fe, Mn relative to the entire section, with the addition of Ba, P, Cd, Ni,

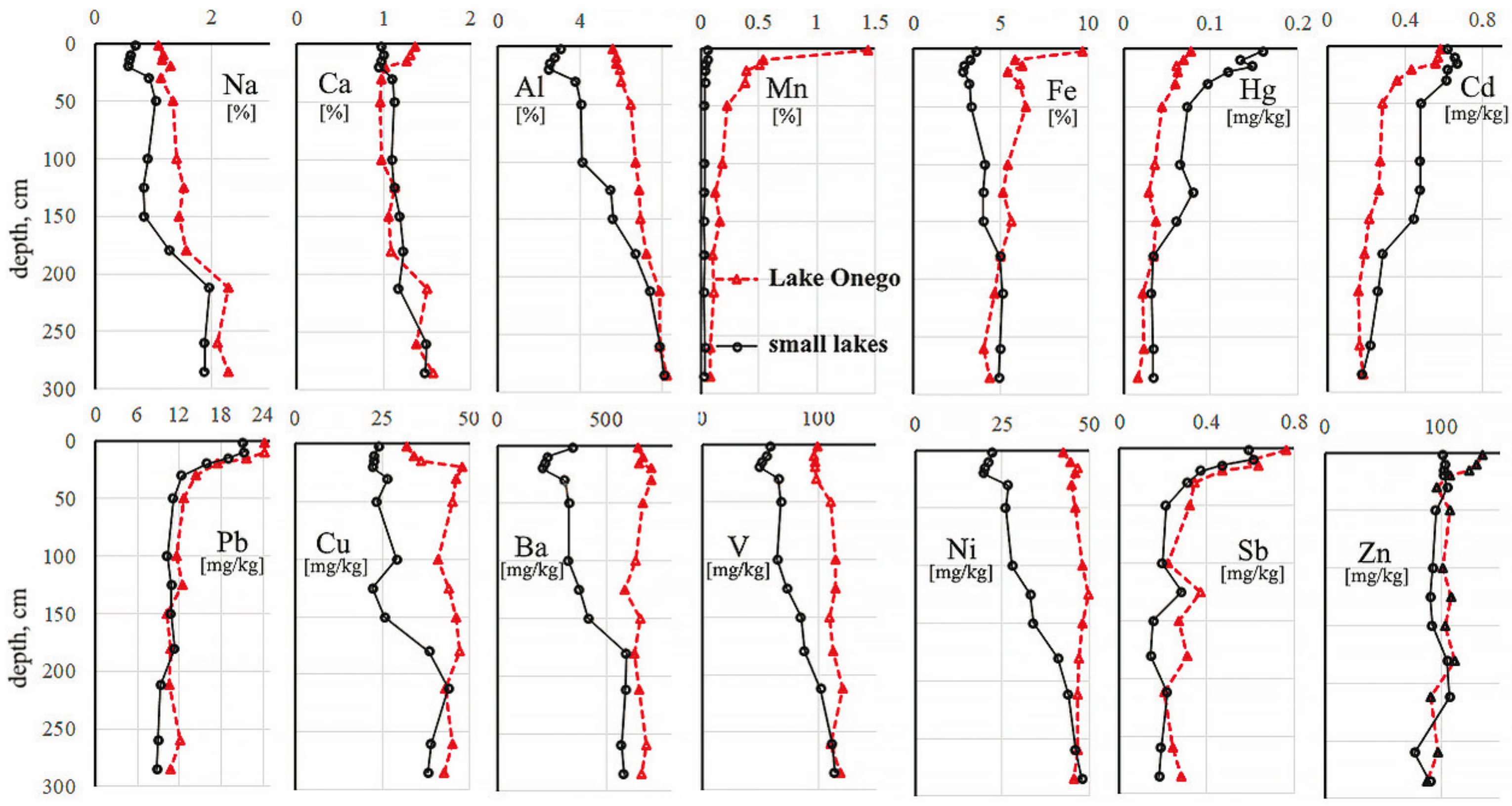


Fig. 10. Vertical distribution of elements in stratified generalized cores of bottom sediments of Lake Onego and small lakes from varved clays to modern sediments (triangle — Lake Onego, circle — small lakes)

Zn, Mo, Ce with a high content of oxygen in the near-bottom waters (1st type of core) at a certain depth from the water — bottom sediment boundary.

For the elements of the third group, the vertical distribution is not characterized by any general trend for different areas of Lake Onego; the sections differ in uneven changes in the elements concentrations by depth. Moreover, the distribution of elements may coincide in the general slope of the spectrum in the 1st and 2nd types of bottom sediments stratification in Lake Onego, differing from small lakes (Fe, Ba, Ni, Zn, Mo, Cr). For another group of studied elements (Fe, Ba, Ni, Zn, Mo, Cr, Si, Ca, Cu, Ti, U), concentrations by depth vary irregularly, with a general tendency for chaotic changes in values within more than two standard deviations both in different areas of Lake Onego and in the bottom sediments cores of small lakes (Si, Ca, Cu, Ti, U). At the same time, for these elements, the uppermost and lowest horizons of bottom sediments practically do not differ in absolute contents.

5. Discussion

Comparison of element concentrations in samples of bottom sediments from different areas of Lake Onego and small lakes showed that in varved clays, the average element contents differ within one standard deviation, and in homogeneous silts, the differences for a number of elements are significant. Significant variations in the elements content in the upper part of the bottom sediments sections of small lakes are associated with the amount of organic matter. This, on the one hand, due to the effect of dilution, reduces the elements concentrations of the terrigenous fraction (Al, Na, K, etc.), on the other hand due to sorption and the formation of complex compounds of a number of metals with organic matter, increases concentrations of, for example, Cd, Sb, Hg, etc. Thus, for example, in Lake Polevskoye, the analysis of the bottom sediments stratification showed that at the stage of "organic accumulation" the content of organic matter was 66 % (C_{org} 29 %, N_{org} 1.6 %, P_{total} 0.1 %, C : N = 29). Bottom sediments have high humidity (98–93 %) and porosity (0.98), low specific mass (1.15 g/cm^3), have a reduced character (–79 mV) and acidic pH = 6.5. The characteristics of organic matter practically do not change down the core, which indicates the stability of the accumulation process of organic matter.

The elements content in the terrigenous fraction of the bottom sediments upper part, for example, Fe was 2 %, Mn (0.01 %), is significantly lower than the values in the upper layer of the Lake Onego bottom sediments (Fe 9–12 %; Mn 0.8–1.1 %) and in OIL varved clays (Fe 7–8 %; Mn 0.05–0.06 %). The concentrations of Cd, Pb, Hg, and Sb are distributed fairly evenly, starting with varved clays and throughout most of the studied vertical time section of bottom sediments, and begin to increase from a depth of ~50 cm to the water-bottom sediment boundary. A similar vertical distribution for the studied elements was revealed for all the considered small lakes. Moreover, the decrease or increase in their absolute values of concentrations correlate well with the amount of organic matter, with the exception of (Cu, Ti). It is known that Zn^{2+} and Cu^{2+} are most intensively involved in migration cycles, and to a lesser extent — Pb^{2+}, Cd^{2+}(Akmukhanova et al., 2018). During the decomposition of organic matter, the variability of Cd and Hg forms allows them to be included in the migration process again. With an undisturbed balance of natural geochemical processes, the geochemistry of cadmium is close to natural, where its affinity with zinc and mercury is manifested (Kabata-Pendias, 2001; Glazovskaya, 2007).

Consequently, in the sections of bottom sediments with an increase in Cd, an increase in Zn to the water-bottom sediment boundary should be recorded, which is observed in the upper part of the Lake Onego bottom sediments. An concentration increase of chalcophilic elements (Zn, Cu, Ni), including Cd, can also be associated with the activity of sulfate-reducing bacteria, the presence of hydrogen sulfide in the upper part of bottom sediments and the sulfides formation. This is possible during the small lakes bottom sediments formation, but an increased concentration in the upper part of the sections is characteristic only of Hg, Sb, Pb, Cd (Kabata-Pendias, 2001). Mn and Fe hydroxides are also an important factor in Cd fixation, for which peak values were detected in the layer of ferromanganese microconcretions in 1st type cores of the Lake Onego bottom sediments.

According to calculations of sedimentation rates by the CRS model in all sections of bottom sediments in different areas of Lake Onego and small lakes, the peak contents of ^{137}Cs in the deep core intervals fall on 1961–1965. The peak activity of ^{137}Cs in this time interval is evidence of the initial contamination of bottom sediments from nuclear tests performed at the Novaya Zemlya test site in 1961–1962. The power of which was equal to 132,710 kiloton or 55.3 % of the power of all atmospheric tests at the Novaya Zemlya test site, including the world's largest nuclear explosion on 10/30/1961 (Nuclear tests…, 2000).

Deposited detritus, inorganic particles and mortmass catch radionuclides from the water and carry them to the bottom. The process occurs synchronously with the continuous redistribution of radioactive elements at the water — bottom sediment boundary and their accumulation by benthos. During the dying of biomass, ^{137}Cs returns to the bottom sediments. On the other hand, most of the ^{137}Cs is concentrated in the uppermost layer of soil and sedimentary loose rocks of the catchment area of lakes, and their destruction leads to secondary contamination of bottom sediments with radionuclides coming from allochthonous particles from catchment basins. Therefore, from the peak values in the upper horizon to the water-bottom sediment boundary, the decrease in ^{137}Cs activity occurs gradually.

6. Conclusions

Comparison of vertical (along cores — the entire Holocene, Late Pleistocene) and lateral (between different areas of Lake Onego) elements distribution with the chemical composition of microparticles and sedimentation rate showed that for a larger part of the studied elements the distribution is fairly uniform, the concentrations increase with depth and reach maximum values in varved clays (Na, Al, Mg, K, Rb, Zr, Th, Be, Li, Nb, V, Sr, Co, Cr, Ta, Cs, Hf, TR (except Eu, Ce)). The geochemical composition of the terrigenous fraction reflects the association of its minerals and is constant for the all bottom sediments cores of Lake Onego and small lakes during the studied time interval (~12,000 years). In homogeneous silts of small lakes in the upper part of the section (from 0 to 600 cm), the increase in organic matter is significantly higher in absolute quantities than in Lake Onego upper section, because amorphous silica composing diatom shells, carbonates composing shell skeletons and macrophyte mortmass are also present in the sediment.

The elements distribution (Mn, Cd, Hg, Pb, Sb, Fe, Ba, Ni, Zn, Mo, Cr, Si, Ca, Cu, Ti, U) varies unevenly with depth, sometimes chaotically within more than two standard deviations, both in different areas of Lake Onego and in bottom sediments of small lakes and has a polygenic genesis. A slight increase towards the water — bottom sediment boundary of the Mn, Fe, Ba, Ni, Cr, U, Mo, and Zn in the Lake Onego bottom sediments is associated with the formation of authigenic minerals (oxides/hydroxides, iron and manganese carbonates, phosphates, iron silicates). The formation of which mainly occurs on redox boundary in the process of diagenesis and in reducing conditions deeper than this boundary. The decrease of these elements content in the upper part of the sections in the small lakes sediments is associated with the presence of significant amounts of organic matter, which, due to the dilution effect, reduces the concentrations of these elements even with their high mobility in sediments during diagenesis. With a high oxygen content in the near-bottom waters (1st type core of Lake Onego) at the redox boundary, the formation of ore layers leads to peak concentrations of Fe, Mn relative to the entire section with the addition of Ba, P, Cd, Ni, Zn, Mo, Ce.

Hg, Pb, Sb are characterized by a uniform unchanging distribution throughout most of the vertical time stage of bottom sediments in all cores, starting with varved clays, and an increase in the contents from a depth of ~ 50 cm to the water — bottom sediments boundary, with an absolute excess of more than 2 times. This is due to the intensive development of industry in general after the World War II in the catchment areas of lakes and an increase in the global atmospheric intake of these elements in the northern hemisphere.

Comparison of the mineral composition in the Lake Onego bottom sediments with the mineral composition of the small lakes bottom sediments showed that the minerals of the terrigenous fraction have a similar composition, dimension, and morphology. Despite the fact that the amount of organic matter (diatoms and macrophyte mortmass) in the upper Holocene part of the small lakes sediments is 2, sometimes 3 times higher, than in Lake Onego. Terrigenous minerals of the small lakes bottom sediments differ only in the composition of fine-scaled, tangled fibrous aggregates of illite and chlorite, which contain iron and magnesium (Fe : Mg = 3 : 1), in contrast to Lake Onego, where these aggregates are represented exclusively by ferruginous varieties. The association of authigenic minerals for bottom sediments is distinguished by the presence of pyrite framboids in small lakes, and for Lake Onego — crystalline aggregates of Fe-phosphate.

Comparison of sedimentation rates in the bottom sediments of various areas of Lake Onego and small lakes located on the territory belonging to Onego Ice Lake showed that the rates of undisturbed sedimentation vary greatly both from lake to lake and across the Onego Lake and vary from 0.05 cm/year to 0.30 cm/year.

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Authors' information:

Vera D. Strakhovenko — strahova@igm.nsc.ru
Natalia A. Belkina — bel110863@mail.ru
Natalia A. Efremenko — efremna@mail.ru
Maxim S. Potakhin — mpotakhin@mail.ru
Dmitry A. Subetto — subetto@mail.ru
Viktor I. Malov — malov@igm.nsc.ru
Ekaterina A. Ovdina — ovdina@igm.nsc.ru

Пространственно-временное распределение элементов в донных отложениях Онежского озера и малых озер, расположенных на водосборной площади Онежского приледникового озера*

В. Д. Страховенко[1,2], *Н. А. Белкина*[3,4], *Н. А. Ефременко*[3], *М. С. Потахин*[3,4,5], *Д. А. Субетто*[4], *В. И. Малов*[1,2], *Е. А. Овдина*[1]

[1] Институт геологии и минералогии им. В. С. Соболева СО РАН, Российская Федерация, 630090, Новосибирск, пр. Академика Коптюга, 3
[2] Новосибирский государственный университет, Российская Федерация, 630090, Новосибирск, ул. Пирогова, 2
[3] Институт водных проблем Севера КарНЦ РАН, Российская Федерация, 185030, Петрозаводск, пр. Александра Невского, 50
[4] Российский государственный педагогический университет им. А. И. Герцена, Российская Федерация, 194486, Санкт-Петербург, наб. р. Мойки, 48
[5] Петрозаводский государственный университет, Российская Федерация, 185910, Петрозаводск, пр. Ленина, 33

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Для изучения позднеплейстоцен-голоценовых донных отложений Онежского озера и малых озер, расположенных на территории Онежского приледникового озера использовались методы ICP-MS, атомно-абсорбционной спектрометрии, рентгенофлуоресцентного анализа, рентгеноструктурного метода, сканирующей электронной микроскопии и гамма-спектрометрический метод. Геохимический состав терригенной фракции определяется совокупностью ее минералов, ассоциация которых в основном одинакова для всех кернов донных отложений Онежского озера и малых озер в течение последних 12 тыс. лет. Верхние части керна донных отложений малых озер отличаются более высоким содержанием органического вещества за счет присутствия более высокого количества створок диатомей, раковин и морт массы макрофитов. Ассоциация аутигенных минералов в донных отложениях отличается присутствием фрамбоидов пирита в малых озерах и агрегатов Fe-фосфата, железистых иллитов в Онежском озере. Сравнение вертикального и латерального распределения элементов с химическим составом микрочастиц и скоростью осаждения показало, что изученные элементы разделились на две группы: для большей части изученных элементов распределение достаточно равномерное, концентрации увеличиваются с глубиной и достигают максимальных значений в различных глинах (Na, Al, Mg, K, Rb, Zr, Th, Be, Li, Nb, V, Sr, Co, Cr, Ta, Cs, Hf, TR (кроме Eu, Ce)). Вторая группа (Mn, Cd, Hg, Pb, Sb, Fe, Ba, Ni, Zn, Mo, Cr, Si, Ca, Cu, Ti, U) имеет неравномерное распределение, меняющееся с глубиной, иногда хаотично в пределах более двух стандартных отклонений, как в разных районах Онежского озера, так и в донных отложениях малых озер. Скорости осадконакопле-

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ния, вычисленные по неравновесному ^{210}Pb атм., в сопоставлении с распределением ^{137}Cs в малых озерах варьируют от озера к озеру, так же как и в различных районах Онежского озера, — в диапазоне от 0.05 см/год до 0.30 см/год.

Ключевые слова: Онежское озеро, малые озера, Онежское приледниковое озеро, донные отложения, минералогия, геохимия, скорость осадконакопления, ^{210}Pb, ^{137}Cs.

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Контактная информация:

Страховенко Вера Дмитриевна — strahova@igm.nsc.ru
Белкина Наталья Александровна — bel110863@mail.ru
Ефременко Наталья Анатольевна — efremna@mail.ru
Потахин Максим Сергеевич — mpotakhin@mail.ru
Субетто Дмитрий Александрович — subetto@mail.ru
Малов Виктор Игоревич — malov@igm.nsc.ru
Овдина Екатерина Андреевна — ovdina@igm.nsc.ru