**Biogeosciences
Discussions**

Biogeochemistry of sediments from restricted exchange environments of Kandalaksha Bay, White Sea, Russian Arctic

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Abstract

The White Sea of Russian Arctic is characterized by extreme diversity of enclosed estuarine systems that are often sites of unique biota. The present study focuses on surface sediments from representative restricted exchange environments of the inner
[5] part of Kandalaksha Bay, adjacent to the Karelian shore of the White Sea. The TOC and n-alkanes distribution study revealed the major input of terrestrial organic matter into the sediments from higher plants and minor presence of autochthonous microbial sources. Metal (Fe, Mn, Cu, Zn, Cr and Pb) forms study showed that metals in sediments occur mainly in a biogeochemically stable mineral-incorporated form, which
[10] comprises up to 98% of total metal content, while labile (acid soluble) and organically bound (alkali soluble) forms make up to 3–11% and 2–12% of total metal content, respectively. Presumably, the major part of both acid soluble and alkali soluble forms is comprised of metals associated with easily soluble amorphous Fe-oxides and bound to sediment organic matter. According to sediment quality guidelines, all trace-metal con-
[15] tents were below the threshold levels. Among sites studied, the heightened contents of bioavailable metal forms are related to sediments enriched in organic matter and/or located within the sea-fresh water barrier zones. The elements studied may be arranged in the following decreasing sequence according to their potential bioavailability: Cu > Zn > Mn > Fe > Cr > Pb. The present study can serve as a basis for comprehen-
[20] sive environmental assessment of the region and objective anoxia prognosis in Arctic ecosystems, while the role of microbial community in element speciation in sediments needs special attention.

1 Introduction

Estuaries and continental shelf areas comprise 5.2% of the earth surface, and only 2%
[25] of the oceans' volume. However, they carry a disproportionate human load (Wolanski, 2007). The White Sea of Russian Arctic is characterized by extreme diversity of

enclosed estuarine systems and biological communities. These areas, which were wildernesses not long ago, are often sites of anthropogenic impacts that expose them to risk (Lisitzin et al., 2010). Hypoxia also occurs in shallow coastal seas and estuaries, where their occurrence and severity appear to be increasing, most likely accelerated by human activities (Rabalais, 2010).

In the recent decades significant research efforts have been undertaken to evaluate concentration of potential contaminants (such as trace metals, oil pollutants, and chemically resistant anthropogenic substances) in sea waters, sediments, and food chains of the White Sea with special attention devoted to shallow areas and estuaries (Koukina et al., 1999, 2001, 2002, 2003, 2005, 2010; Peresypkin and Romankevich, 2010; Shaporenko et al., 2005). Very little is known, however, about the carriers and transport modes of these contaminants or their response to estuarine conditions. The upper sediment column in estuarine and coastal environments can be regarded as a slowly stirred reactor to which substrates are added at the top and mixed downward (Martin, 2010). Major and trace element speciation is essential in processes such as the toxity and bioavailability of pollutants in natural systems (Gerson et al., 2008, Krishnamurti, 2008). Since estuarine and shelf sediments are unique traps for elements entering the marine environment, the present study focuses on the sediments of the inner part of Kandalaksha bay, adjacent to the Karelian shore of the White Sea. Due to the endogenous crustal uplift (4 mm per year an average), this bay contains a continuum of shallow environments, ranging from estuaries of different types to separating basins where water exchange is severely restricted. The evolution of sediments here is caused by specific depositional conditions, which are strongly affected by small-scale hydrological, hydrodynamic and hydrochemical processes unique for each particular area, of which the hypoxia is of most importance (Koukina et al., 2010). Biogeochemical characterization of sediments from such unstable environments can serve as a basis of environmental assessment of the region and allows some deductions as to carriers, transport modes and potential bioavailability of major and trace elements entering and within these different systems. Hence, in the work presented TOC, *n*-alkanes and

metal (Fe, Mn, Cu, Zn, Cr and Pb) forms distribution was determined in surface sediment samples from representative small exchange environments of the Karelian shore.

2 Materials and methods

2.1 Study area and sampling

2.1.1 Environmental setting

The White Sea is a sub-Arctic inland sea (Fig. 1). It is the only Arctic sea with the major part of its basin south to the Polar Circle. The climate of the region is transitional from oceanic to continental, with long severe winters and cool summers. The period of ice cover lasts, on average, from November until May. The total area of the White Sea is approximately $90\,000\,\mathrm{km}^2$, with a water volume of some $6000\,\mathrm{km}^3$. The average bottom depth is 67 m, with a maximum depth of 350 m (Glukhovsky, 1991). Despite its small area, the White Sea is characterized by a relatively large discharge of river water – around $180\,\mathrm{km}^3$ per year (Dobrovolsky and Zalogin, 1982). This discharge is spread between four major bays: Mezensky Zaliv (Mezen Bay), Dvinskoy Zaliv (Dvina Bay), Onegsky Zaliv (Onega Bay) and Kandalakshsky Zaliv (Kandalaksha Bay). The first three bays are located at the mouths of the major rivers of the White Sea: the Mezen, Severnaya Dvina and Onega, respectively.

The deepest bay, Kandalaksha Bay, is a wide estuary with evenly distributed freshwater discharge (Pantiulin, 2001). A pronounced tidal asymmetry with an ebb tide lasting twice as long as the flood tide is characteristic of the area. The Karelian coastline of Kandalaksha bay forms a continuum of small bays of 1–35 km in length. Shallow sea areas and enclosed estuarine systems were found to be characterized by extreme diversity of biological communities as well as very active fronts and biogeochemical barriers creating small scale variability in hydrodynamic, lithological and geochemical patterns (Koukina et al., 2003).

The major geological feature of the region is modern endogenous crustal uplift of 4 mm per year an average (Oliunina and Romanenko, 2007). Due to this process numerous small bays, lagoons and straits are isolating from the sea with further transformation into brackish and fresh water lakes. These reservoirs named separating basins are characterized by specific hydrological and hydrochemical regimes and contrast oxidizing conditions often complicated by anoxia zones occurrence (Shaporenko et al., 2005).

The present study focuses on four small basins along the Karelian shore of Kandalaksha Bay: Chernorechenskaya Bay (the inner part), Kislosladkoe Lake, Cape Zeleny Lake, and Porchalische lagoon (Fig. 2).

Chernorechenskaya Bay, located at the mouth of the Chernaya River, is 2 km long and consists of upper and lower basins with maximum depths of 5 and 10 m, respectively. The basins are separated from each other by shallow bars. It is a typical small estuary characterized by permanent fresh-water input throughout the year, resulting in significant vertical and horizontal salinity gradients.

Kislosladkoe Lake, located 2 km to the east from Primorsky village, is oval shaped with 180 m length and 100 m width. It is a typical separating basin isolated from Velikaya Salma strait by an uplift of two underwater rock bars. There is an insignificant surface water exchange with Kandalaksha Bay and the lake. The swampy southern shore is characterized by insignificant, but constant, fresh water input provided by a small stream.

The separating lake at Cape Zeleny is located 6 km to the south from Primorsky village. It is round shaped with 200 m length and 120 m width. The former lagoon was isolated from Kislaya Bay by a rock bar. The small strait still provides a water exchange between lake and bay. At the highest flood tide sea water enters the lake, while during the rest of the time the lake water is discharged into the bay. There is no permanent fresh water input, while seasonal fresh water outflow from the southern shore may occur.

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Porchalische lagoon is a littoral pool located 300 m to the north at the marsh runoff. During the flood tide the pool is encroached by sea water, during the ebb tide – fully filled with fresh water.

2.1.2 Sampling

Ten surface sediment samples were collected between 28. August–10. September 2008 in the littoral zone of Karelian shore of Kandalaksha Bay in small exchange environments Kislosladkoe Lake, Cape Zeleny Lake, Chernorechenskaya Bay and Porchalische lagoon (Fig. 1).

Sediment samples were obtained during the ebb tide, with a 0.2 l plastic box-corer designed at the P. P. Shirshov Institute of Oceanology. The upper layer (0–6 cm) of the samples was retrieved with stainless steel spatulas, transferred into pre-cleaned polyethylene containers and frozen until analyses. Where present, surface oxic yellowish layer (0–3 cm) was retrieved and collected separately. Sampling, sample transportation and preparation procedures were carried out using standard clean techniques described elsewhere (Koukina et al., 1999; Loring and Rantala, 1992).

2.2 Methods

2.2.1 Total organic carbon (TOC) and carbonates analyses

From each station, 100–150 g of sediment sample was dried at 60 °C, ground and homogenized.

Total organic carbon (TOC) and carbonates contents were determined in dry sediment samples on Shimadzu analyzer TOC Vcph (Shimudzu Co.) in the Ocean Chemistry Laboratory of P. P. Shirshov Institute of Oceanology of RAS.

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2.2.2 *n*-alkanes analyses

The *n*-alkanes were isolated from dry powdered sample by 45 min hexane extraction in Branson 1210 ultrasonic bath (Branson Ultrasonic B.V. Co) preceded by 15 min degassing. The extract obtained was filtered through GF/F glass fiber filters under vacuum. The solvent was evaporated at 35 °C in Yamato RE-52 vacuum rotor vaporizer. To remove dissolved sulfur, the extract obtained was passed through an activated metallic copper column, evaporated in a nitrogen flow and stored in a refrigerator at +5 °C until instrumental analysis. Further determination of *n*-alkanes contents in the extracts was carried out on Shimadzu GCMS-QP 5050 chromatographic mass spectrometer (Shimudzu Co.) in the Ocean Chemistry Laboratory of P. P. Shirshov Institute of Oceanology of RAS.

2.2.3 Metal analyses

In order to determine acid soluble (labile), organically bound and total contents of Fe, Mn, Cr, Pb, Zn and Cu, samples were parallel treated by 25% acetic acid (CH_3COOH), 0.1 M sodium pyrophosphate ($Na_4P_2O_7 \cdot 10H_2O$) and aqua regia ($HNO_3 : HCl = 1 : 3$), respectively. The difference between amounts of acid soluble and total metal contents was considered a measure of mineral incorporated (acid insoluble) metal form.

To isolate the acid soluble metals, 15 ml of 25% acetic acid was added to 1.1 g of dry sample in a polypropylene vial and shake in a mechanical shaker for 6 h. The extract with sediment was then filtrated into a 25 ml glass volumetric flask. The sediment on the filter was washed with 10 ml of distilled water, the wash water added to the flask.

To isolate the organically bound metals, 15 ml of 0.1 M sodium pyrophosphate was added to 1.1 g of dry sample, shake for 15 min in a mechanical shaker and left for 24 h. The extract with sediment was then filtrated into a 25 ml glass volumetric flask. The filter was washed with 10 ml of 0.1 M sodium pyrophosphate, the wash liquid added to the flask.

For total metal content analysis, 0.5 g of dried powdered sample was kept in the oven at 300 °C until constant weight. Afterwards, the sample was objected to a triple successive treatment by aqua regia ($HNO_3 : HCl = 1 : 3$) with evaporating. After the last evaporating, residual sediment was objected to dissolution in 1 M HNO_3 with heating.

Further determination of metal contents in the extracts was carried by an atomic absorption spectrometer (AAS) Hitachi 180–8 in the Analytical Centre of Lomonosov Moscow State University. The relative accuracy for AAS determinations was within the standard deviations of the certified sediment reference material SDO-1 (Berkovitz and Lukashin, 1984).

3 Results and discussion

3.1 Sediment distribution and biogeochemical characteristics

3.1.1 Sediment type distribution

Karelian shore sediments can be divided in to two main lithological facies according to sedimentary conditions in the White Sea: the facies of coastal zone and the facies of bays formed by the rugged cost (Lisitzin et al., 2010). In the coastal zone, tidal and wind generated currents form coarse sediments, of which well sorted fine-grained sands are of most importance. In the small bays of rugged coast, the hydrodynamic and thus sedimentary conditions are very calm, leading to accumulation of fine-grained silty material (Koukina et al., 2003). These sediments are mainly comprised of aleurite silts, which often have a high content of coarse fragments.

Textural studies indicate that sediment distribution along the studied part of the Karelian shore is a patchwork of brownish silty sands, brownish and grayish sandy aleurite silts, and fine-grained brownish and grayish aleurite silt deposits. Most of sediments are characterized by a yellowish oxic surface layer 1–3 cm thick. The most fine-grained organic-rich and sometimes hydrosulfuric sediments are found in separating basins (Koukina et al., 2010).

3.1.2 Total organic carbon and carbonates distribution

Sedimentary organic content showed great variability, ranging from 0.3% to 18.7% for TOC (an average 4.5%) (Table 1).

Among sites studied, the lowest TOC sediment content is related to the mouth of Chernaya River in Chernorechenskaya Bay (Fig. 1). At this site the loose surface yellowish layer showed twice lower TOC content of 0.4% in comparison to the underlying grayish silty sediment (1%) (st. 30, 31). This might be due to an enhanced destruction (oxidation) of newly deposited organic matter characteristic for surface oxic layer (Martin, 2010). Although, estuarine currents may transport the loose mud within the water mixing zone, so that the surface muddy layer may not be necessarily bound to the subsurface sediment.

Within Cape Zeleny Lake, the strait bed sediment sample exhibited the TOC content of 2.1% (st. 12). In the western shallow part of the lake, sediment comprised of grayish silt with TOC of 1.6% was overlied by an oxic layer with the twice higher TOC content of 3.4% (st. 13, 14). Sediments from the southern part of the lake, influenced by seasonal fresh water input and hence terrigenous organic matter supply, were mostly enriched in TOC (4.9% and 3.9% for oxic and underlying layer, respectively (st. 15, 16)).

In Kislosladkoe Lake, the sediment collected in the eastern part of the lake near the rocky bar strait (st. 17, 18), exhibited a thick (3 cm) organic rich oxic layer (8.3% of TOC) underlying by a poor in organic matter dark colored silty sand (0.3% of TOC). The surface sediment is most probably newly formed under the calm hydrodynamic of separating basin, while the subsurface sand originates from the times when the basin had a free exchange with Velikaya Salma Strait.

The TOC maximum content (18.7%) is related to Porchalische lagoon, where the fine-grained silt with hydrosulfuric smell was collected. The marine algae brought into the lagoon by storms cannot survive under the stress from regular tidal sea-fresh water change (Vetrov and Peresypkin, 2009). Further deposition and decomposition of the algal mass might contribute to a high organic matter accumulation rate and hence formation of anoxic sediments.

Sediment inorganic carbon, presumably supplied by carbonates (0.3–2%), was uniformly low in the samples studied (Table 1). The extreme high (for the region studied) carbonate content of 50% was found in the strait connecting Cape Zeleny and Kislaya Bay in the vicinity of a large boulder (st. 12). The strait bed is comprised of silty rubble and silty sand with a high content of shell residues coming out of mussel colony inhabiting the boulders.

3.1.3 *n*-alkanes distribution

The total *n*-alkanes content ranged from $0.2 \, \mu g \, g^{-1}$ to $7.4 \, \mu g \, g^{-1}$ (mean $3.3 \, \mu g \, g^{-1}$) (Table 1). These values are considered to be relatively low for the area studied (Peresypkin and Belyaev, 2009).

Spearman correlation coefficient revealed strong positive correlation ($r_s = 0.88$) between TOC and *n*-alkanes content for the sediments studied.

The *n*-alkanes distribution (Fig. 2) relative to hydrocarbon chain length showed the maximums in C_{23}–C_{35} zone in the most of samples studied marking the major input of organic matter from terrestrial plant remains. The terrigenous hydrocarbons make up to 80% of total *n*-alkanes content. The mean values of the low-molecular to high-molecular homologues ratio ($\sum C_{12}$–$C_{22} / \sum C_{23}$–C_{35}) of 0.45 (ranging from 0.1 to 1.1) and CPI (Carbon Preference Index) of 6.38 (ranging from 2.74 to 11.9) also contribute to the permanent terrigenous organic matter input into the sediments within the area studied (Table 1). The mean i-C_{19}/i-C_{20} value of 0.89 (ranging from 0.22 to 1.48) may indicate that transformation of the original organic matter in sediments studied often occurs under redox conditions, which are mostly pronounced in Porchalische lagoon (st. 26).

In some samples (st. 12, 30, 31), the elevated content of low-molecular hydrocarbons C_{14}–C_{17} with clear maximum at C_{17} marks an autochthonous microbial source of organic matter. At these sites, the total *n*-alkanes content in sediments was low (0.5–$1 \, \mu g \, g^{-1}$), and the sum of low molecular homologues ($\sum C_{12}$–C_{22}) made up to 45–60%. The found *n*-alkanes distribution is typical for the sediments covered by bacterial mats

(e.g. purpur sulfur and green cyanobacteria species) (Peresypkin and Belyaev, 2009). The highest C_{17} peak (27%) is related to the upper oxic sediment layer in Chernaya River estuary (st. 30), where the lowest TOC content of 0.4% was determined.

The sample from Porchalische lagoon (st. 26) is characterized by highest TOC (18.7%), $\sum C_{23} - C_{35}$ (> 80%) and C_{27} peak (up to 40%), while relatively low total n-alkanes (5.87 µg g^{-1}) content and lowest i-C_{19}/i-C_{20} index (0.22) among sites studied. This indicates the significant terrigenous organic matter input from terrestrial plant remains (despite the algal mass supply characteristic for this site), and their decomposition under redox conditions. Hence, the significant part of organic matter might be comprised of organic substances other than n-alkanes which require special investigation.

3.2 Metals in sediments

3.2.1 Abundance and distribution of metals in surface sediments

Table 2 shows the metal contents distribution in the Karelian shore sediments.

Fe is a sediment indicator of Fe-rich aluminosilicates, Fe-rich heavy minerals, and hydrous Fe oxides. The total Fe in Karelian shore sediments was relatively low and varied within the range of 0.4–2.3% in the samples studied. Total Mn ranged from 26 to 150 µg g^{-1}, and total Cr ranged from 11 to 68 µg g^{-1}, while Mn and Cr distribution was similar to that of Fe (Spearman correlation coefficient r_s was 0.92 and 0.98, respectively). The elevated contents of Fe, and thus of Mn and Cr, were found in the fine-grained silts from Cape Zeleny Lake and Chernorechenskaya Bay (Table 2, st. 13–16, 30–31). These sites experience a significant input of terrestrial material from permanent and/or seasonal fresh water discharge that supply Fe and Mn oxides. The upper centimeters of these sediments have an oxic "cap" just below the sediment-water interface, where Fe and Mn oxides precipitate (Martin, 2010). Cr, being a siderophile element, may be both associated with Fe-Mn bearing minerals and precipitated with Fe and Mn oxides that can lead to enrichments in fine-grained solids of surface sediments. However, at some sites, the subsurface sediments were slightly enriched in Fe, Mn and

Cr comparing to surface oxic layer (st. 15–16, 30–31). That can be attributed to the post-depositional diagenetic effects of Fe-Mn cycling both at and near the sediment-water interface (Loring et al., 1998). Sediment resuspension and subsequent reaction and transport in the water column can be an important mechanism for redistribution of major and trace contaminant metal.

Total Pb, Cu and Zn varied in the ranges 1–6, 3–60, and 30–240 µg g^{-1}, respectively. Total Pb content was uniformly low and significantly correlated with total Fe ($r_s = 0.69$). Total Cu was positively correlated with TOC ($r_s = 0.57$) with clear content maximum in organic rich sediment from Porchalische lagoon (59 µg g^{-1}). The sedimentation of Cu in the system is to a higher degree bound to organic matter sedimentation processes than for other metals studied (Koukina et al., 1999, 2001, 2010). Total Zn showed no pronounced affinity to major and trace elements studied but exhibited enrichments in surface sediments of Cape Zeleny Lake (st. 12) and Porchalische lagoon (st. 26), subsurface sediments from Cape Zeleny (st. 14, 16) and especially Kislosladkoe Lake (240 µg g^{-1}, st. 18). According to the structure of shallow-water marine sediments, below the oxic layer is a region of Fe and S reduction. Below this layer – if the supply of organic matter supports extensive sulfate reduction – is a layer of elevated dissolved H_2S (Martin, 2010). Many trace metals – and Zn as a chalcophile element – both form insoluble sulfides and tend to sorb on to precipitating Fe oxides. Hence, they are released to pore waters when Fe oxide reduction occurs, but tend to be immobilized by precipitation as sulfides. The sporadic enrichments in Zn may be also attributed to mineralogical composition of the sediment and hence anomalous concentrations of detrital heavy minerals containing the element. Thus, Zn may preferentially concentrate in some of the rock-building minerals, characteristic for Karelian shore, for example, ferro-magnesium silicates (Koukina et al., 2003). At the same time, anthropogenic materials (e.g. Zn as trace heavy metal) can both be present in the sediments from deposition in the past and can arrive with current deposits. However, according to effects range-low (ERL) and effects range-median (ERM) sediment quality guidelines for trace metals (Long et al., 1995), all found contents were below the ERM levels generally suggested

to have potential adverse biological effects.

3.2.2 Metal forms in surface sediments

Trace metals are introduced into coastal sediments as constituents of, or in association with, solid inorganic and organic particles supplied from natural and anthropogenic sources or derived from solution (Loring et al., 1998). The most important metal carriers within these sediments are aluminosilicate clay minerals, Fe-Mn oxides, marine and terrestrial organic materials, carbonates, and detrital heavy minerals (Postma, 1980; Foerstner and Wittmann, 1981). Thus, because the metal is distributed over different phases, a simple measurement of total concentrations of the metal is inadequate to assess its bioavailability (Wolanski, 2007). It is necessary to measure the metal in the various phases and this is usually done using selective or/and sequential extraction (Perin et al., 1997; Riedel and Sanders, 1998; Szefer et al., 1995).

The previous sequential extraction studies of Karelian shore sediments showed that metals occur mainly in a biogeochemically stable mineral-incorporated form, which comprises 77–99% of total metal content (Koukina et al., 2001, 2010). These are metals incorporated into aluminosilicate lattices, bound to resistant iron and manganese minerals or organic compounds, integrated with detrital heavy minerals or discrete hydroxides, carbonates and sulfides.

In this work, the two selective extractions were performed in order to assess potentially most bioavailable metal fractions in sediments being labile (acid soluble) and organically bound (alkali soluble). The labile (weakly bound) part of total metal content was extracted using the 25% acetic acid. The acetic acid removes metals held in ion exchange positions, easily soluble amorphous compounds of iron and manganese, carbonates and those metals weakly held in organic matter (Loring and Rantala, 1992). The proportion of the total metal removed by the extraction is defined as acid soluble (non-detrital) metal fraction in sediments. The 1 M sodium pyrophosphate (pH 10) extract was supposed to remove the organically bound metals from sediments (Beckett, 1989). Organic matter could play a critical role in concentrating metals via ligand

binding (Gerson et al., 2008, Naidu et al., 1997). Organic substances of different origin are first subjected to numerous biotic and abiotic diagenetic transformations in the surficial sediments, while associated elements may become more bioavailable. 1 M sodium pyrophosphate is known to mobilize also some part of easily soluble amorphous Fe-oxides and hence the elements associated with (Vorobyova, 2006).

The amounts of metals extracted by 25% acetic acid and 1 M sodium pyrophosphate are given in Table 2. For Pb, contents of both labile acid soluble and organically bound alkali soluble forms were negligible or below the detection limit.

The amounts of labile acid soluble form varied within the ranges of 146–3030 $\mu g\,g^{-1}$ for Fe, 3–25 $\mu g\,g^{-1}$ for Mn, 1–3 $\mu g\,g^{-1}$ for Cr, 1–2 $\mu g\,g^{-1}$ for Cu, and 3–12 $\mu g\,g^{-1}$ for Zn. This form made up 3–15% (an average 6.1%) of total contents for Fe, 2–27% (10.2%) for Mn, 0.5–5.5% (3.3%) for Cr, 3–27% (10.7%) for Cu and 1–25% (8.6%) for Zn (Fig. 3).

The amounts of organically bound form varied within the ranges of 47–2390 $\mu g\,g^{-1}$ for Fe, 1–19 $\mu g\,g^{-1}$ for Mn, 1–2 $\mu g\,g^{-1}$ for Cr, 1–3 $\mu g\,g^{-1}$ for Cu, and 2–19 $\mu g\,g^{-1}$ for Zn. This form made up 1–14% (an average 6.4%) of total contents for Fe, 0.5–18% (4.1%) for Mn, 0.5–3% (1.6%) for Cr, 3–2% (11.7%) for Cu and 1–21% (6.9%) for Zn (Fig. 4).

The relative percent content of labile acid soluble form (in relation to total metal content) significantly exceeded these of organically bound alkali soluble form at all sites for Mn, and at most of the sites for Cr and Zn (Figs. 3 and 4). For Fe and Cu, acid soluble form slightly exceeded the alkali soluble form, except sites where sediments were mostly enriched in TOC (st. 17 and 26, 8.3% and 18.7% of TOC, respectively). In these organic rich sediments, the content and the part of organically bound Fe, Cu, and sometimes Zn (st. 26) were at least twice higher than these of labile metals.

For Fe, the distribution of both labile and organically bound forms in the samples studied is to a great extent a function of total Fe content ($r_s = 0.71$–0.83), while relative enrichments in labile and organically bound Fe were related to the sediments from Cape Zeleny Lake (st. 12, 15, 16) and especially to the subsurface sediments from Chernaya River estuary (st. 31).

Labile, organically bound and total Cr was significantly positively correlated with respective forms of Fe ($r_s = 0.67$–0.98). Labile and organically bound Mn distribution did not reveal any positive correlations with other elements studied. However, enrichments in organically bound and, to a higher extent, in labile Mn were related to Cape Zeleny Lake strait bed (st. 12), organic rich surface sediment from Kislosladkoe Lake (st. 17), and subsurface sediment from Chernaya River estuary (st. 31). Strong positive correlation is revealed between organically bound forms of Zn and Cu ($r_s = 0.85$), which were both positively correlated with organic carbon ($r_s = 0.62$–0.63), while labile Zn exhibited even stronger correlation with TOC ($r_s = 0.82$).

An average, acetic acid and sodium pyrophosphate seem to release comparable amounts of metals from the sediments (3–11% and 2–12% of total metal content, respectively). This might be due to a poor selectivity of these reagents. Thus, both acetic acid and sodium pyrophosphate are able to remove metals weakly held in organic matter and associated with easily soluble amorphous Fe-oxides.

Assuming that the determined amounts (parts) of acid soluble and alkali soluble forms could be a measure of potential metal bioavailability in sediments, the elements studied may be arranged in the following decreasing sequence: Cu > Zn > Mn > Fe > Cr > Pb.

Among sites studied, the elevated content of both bioavailable forms of most metals studied is related to samples 12, 17, 26, 31. The surface silts from Kislosladkoe Lake (st. 17) and Porchalische lagoon (st. 26) experience the significant supply of terrestrial organic matter and are mostly enriched in TOC. The surface silty sand collected from the bed of the strait connecting Cape Zeleny Lake and Kislaya Bay (st. 12) experiences the regular sea-fresh water change. The subsurface silt collected in the vicinity of Chernaya River mouth (st. 31) is located within the estuarine water mixing zone. In both samples (12 and 31), the clear imprint of the microbial organic matter was detected. Hence, the role of microbial community in element speciation in sediments needs special study.

4   Conclusions

The evolution of sediments from the restricted exchange environments of the Karelian shore is strongly affected by small-scale hydrological and hydrodynamic processes unique for each particular area, of which the separating process is of most importance.

The TOC and *n*-alkanes distribution showed that sediments studied tend to be terrigenous with major input of organic matter from terrestrial plant remains and minor presence of autochthonous microbial sources. Sedimentary organic content showed great variability, ranging from 0.3% to 18.7% for TOC (an average 4.5%) and positively correlated with total *n*-alkanes content ($r_s = 0.88$).

According to sediment quality guidelines, all trace-metal contents were below the threshold levels. Total Pb was uniformly low in sediments studied. Total Mn and Cr distribution followed that of Fe ($r_s = 0.92$–0.98). Total Cu distribution was close to that of organic carbon. Total Zn showed the sporadic enrichments presumably attributed to variances in sediment composition.

Metals occur mainly in a biogeochemically stable mineral-incorporated form, which comprises up to 98% of total metal content in sediments. The comparative study of two most bioavailable metal forms being labile (acid soluble) and organically bound (alkali soluble) showed that acetic acid and sodium pyrophosphate release comparable amounts of metals from the sediments being 3–11% and 2–12% of total metal content, respectively. The relative part of labile form exceeded that of organically bound at all sites for Mn and at major sites for other elements studied, while the organically form dominated in sediments enriched in TOC.

Presumably, the major part of both acid soluble and alkali soluble forms is comprised of metals associated with easily soluble amorphous Fe-oxides and bound to sediment organic matter. Among sites studied, the elevated contents of bioavailable metal forms are related to sediments enriched in organic matter and/or located within the sea-fresh water barrier zones.

According to their potential bioavailability, the elements studied may be arranged in the following decreasing sequence: Cu > Zn > Mn > Fe > Cr > Pb.

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**Table 1.** TOC, carbonates and *n*-alkanes distribution in surface sediments.

Study area	Station	Layer (cm)	Sediment type	CaCO$_3$ %	TOC %	*n*-alkanes µg g^{-1}	i-C$_{19}$/ i-C$_{20}$	CPI	$\sum$C$_{12}$+C$_{22}$/ $\sum$C$_{23}$+C$_{40}$
Cape Zeleny Lake	12	0–1	silty sand	50.7	2.10	0.52	0.71	3.48	1.10
	13	0–1	silt	0.38	3.40	3.82	1.11	7.82	0.16
	14	1–6	silt	0.33	1.60	2.11	1.37	6.40	0.19
	15	0–1	silt	0.30	4.90	5.90	0.42	6.59	0.24
	16	1–6	silt	0.58	3.90	7.37	0.61	6.69	0.15
Kislosladkoe Lake	17	0–3	silt	1.97	8.30	5.24	1.15	9.57	0.13
	18	3–6	silty sand	0.30	0.25	0.24	1.30	2.74	0.59
Porchalische lagoon	26	0–1	silt	0.83	18.7	5.87	0.22	11.9	0.10
Chernorechenskaya Bay	30	0–1	silt	2.07	0.40	1.11	0.53	4.70	1.06
	31	1–3	silt	0.32	1.00	0.89	1.48	3.87	0.78
	Mean	–	–	5.77	4.46	3.31	0.89	6.38	0.45

Table 2. Acid soluble (labile), alkali soluble (organically bound) and total metal distribution in surface sediments ($\mu g\,g^{-1}$).

| St.	Pb total	Cu acid sol.	Cu alkali sol.	Cu total	Zn acid sol.	Zn alkali sol.	Zn total	Cr acid sol.	Cr alkali sol.	Cr total	Mn acid sol.	Mn alkali sol.	Mn total	Fe acid sol.	Fe alkali sol.	Fe total
12	2	1	1	3	3	4	159	< 0.5	< 0.5	12	7	2	26	286	252	3560
13	6	2	2	18	5	5	63	2	1	68	4	1	150	756	665	22 710
14	1	2	1	13	5	4	151	1	< 0.5	50	4	< 0.5	115	594	509	17 400
15	6	1	1	8	6	4	31	3	2	49	5	2	88	1504	1595	19 240
16	6	1	< 0.5	13	7	4	61	2	1	52	4	1	106	1900	1710	20 500
17	3	1	3	14	8	7	32	1	1	21	9	5	54	330	1145	8180
18	3	1	1	5	3	2	241	1	< 0.5	15	3	1	44	146	47	5560
26	1	2	3	59	12	19	190	< 0.5	< 0.5	43	4	1	79	357	630	12 890
30	5	1	1	12	5	4	128	1	< 0.5	45	5	1	80	775	418	16 100
31	5	1	1	12	5	3	128	2	1	51	25	19	102	3030	2390	20 500
Mean	4	1	1	16	6	6	118	1	1	41	7	3	85	968	936	14 664
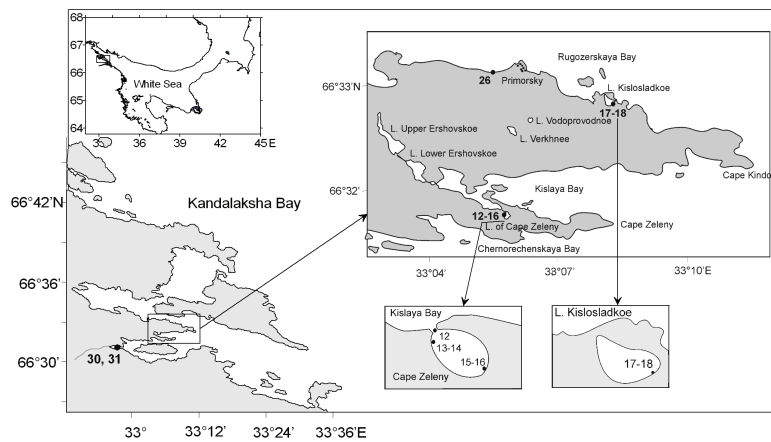
Fig. 1. Map of Kandalaksha Bay of the White Sea showing the location of the sampling stations.
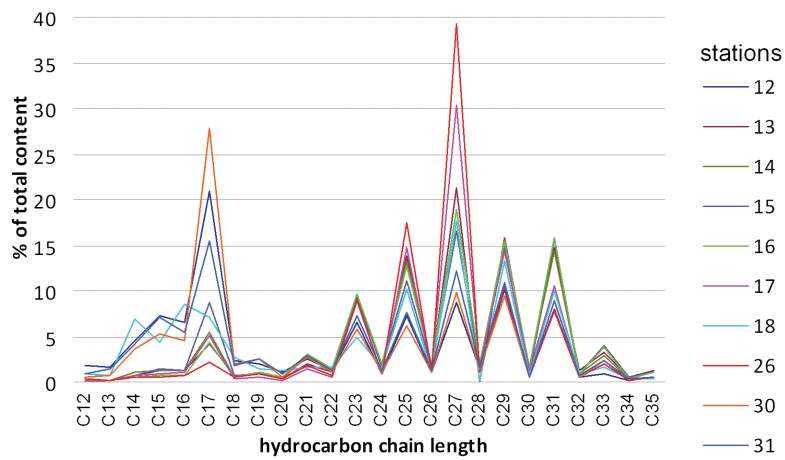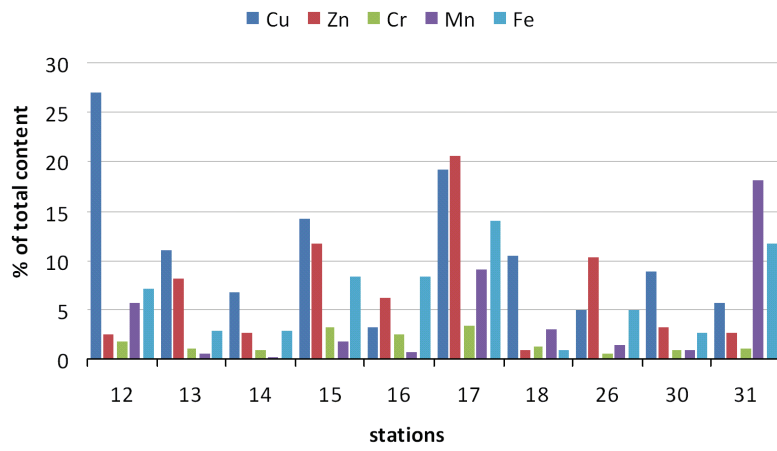
Fig. 2. The distribution of *n*-alkanes in surface sediments.

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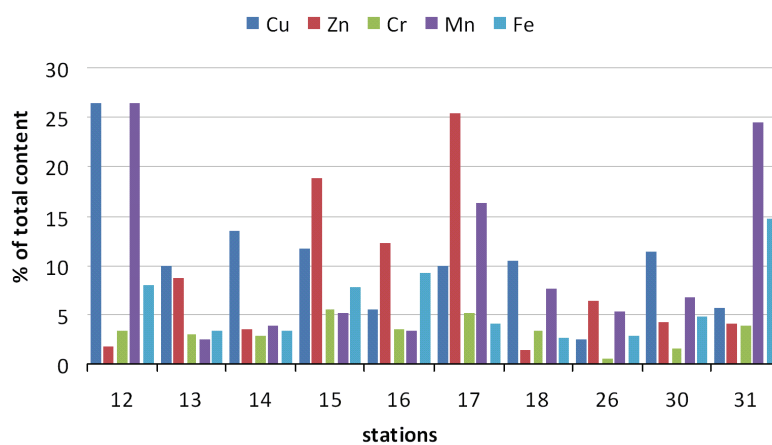
Fig. 3. The distribution of acid soluble (labile) metals in surface sediments.

Fig. 4. The distribution of alkali soluble (organically bound) metals in surface sediments.

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