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Ecological Research of Arctic Restricted Exchange Environments (Kandalaksha Bay, White Sea, Russian Arctic)

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1. Introduction

Estuaries and continental shelf areas comprise 5.2% of the earth surface, and only 2% of the oceans' volume. However, they carry a disproportionate human load (Wolanski, 2007). Hypoxia also occurs in shallow coastal seas and estuaries, where their occurrence and severity appear to be increasing (Rabalais, 2010).

The Arctic has come under intense scrutiny by the scientific community in recent years. This is due to the key role played by the region in the variability of the world ocean and, hence, the Earth's climate, its vast and still not fully realized natural resources, and rapidly increasing technogenous load on the environment (Shapovalov, 2010). The White Sea of Russian Arctic (the only Russian inland sea) is characterized by extreme diversity of enclosed estuarine systems that are inhabited by unique biota (Krasnova, 2008, Lisitzin et al, 2010). These environments, which were wildernesses not long ago, are often sites of anthropogenic impacts that expose them to risk (Peresypkin & Romankevich, 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 enclosed estuarine systems (Koukina et al., 2001, 2010, Savenko, 2006). Most of these areas were found to be characterized by very active fronts and biogeochemical barriers creating small scale variability in hydrodynamic, lithological and geochemical patterns that significantly complicates the differentiation of sites of natural element accumulation from sites of anthropogenic contamination (Koukina et al, 2003, Pantiulin, 2001).

The major geological feature of the coastal zone of the White Sea is modern endogenous crustal uplift of 4 mm per year an average (Oliunina & 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 unique ecosystems named separating basins (in a wider sense, restricted exchange environments) were not sufficiently studied until recent time due to the tiny (to oceanographic ranges) sizes and sea-isolated setting. Characteristic for such reservoirs specific hydrological and hydrochemical regime was earlier observed in the relict Arctic lake Mogil'noe located on the Kil'din Island of the Barents Sea (Sapozhnikov et al, 2001). The study of two separating lakes of Kandalaksha Bay

(Kislosladkoe Lake and Cape Zeleny Lake) first revealed the specific features of separating process within Karelian coastaline of Kandalaksha Bay of the White Sea (Shaporenko et al, 2005). These reservoirs being separating basins of different isolation phase were shown to be characterized by sharp water column stratification, extreme values of hydrological and hydrochemical parameters and ultra-contrast oxidizing conditions complicated by subsurface oxygen maximums (O_2>20 mg/l) and anoxic hydrosulfuric (H_2S>90 mg/l) zone occurrence in the central bottom depressions. The complex of environmental changes occurring under separation, of which the anoxia and its consequences are of most hazarding, often leads to the disturbance within the ecosystem. Thus, in the separating basins under investigation the mass extinction of marine biota and simultaneous microbial community extension were observed (Peresypkin & Belyaev, 2009, Vetrov & Peresypkin, 2009). The further study of such restricted exchange environments is essential for comprehensive environmental assessment of the region as well as for objective anoxia prognosis in Arctic ecosystems.

Sediments in separating basins are unique traps for elements entering these aquatic environments. 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). The comparative biogeochemical study of Karelian shore coastal basins showed the pronounced enrichment of sediments from separating bays in clay fraction, organic matter and in nutrients and metals in comparison to the neighboring open shallow sea (Koukina et al, 2003, 2006). Further study of the region revealed the extreme high total Fe (160000 µg/g) as well as enhanced content of labile (acid soluble) Fe, Mn and Cr in sediments from central parts of two separating lagoons of Chernorechenskaya Bay (Koukina et al, 2010). Since all previously made biogeochemical assessments of the Karelian shore showed no significant contamination, the enrichments of sediments from separating basins (sometimes reaching the artifact concentrations) were preliminary related to the natural accumulation of organic matter, Fe and trace metals and, especially, their labile forms within the solid sediment phase, and this may occur due to the specific conditions of separating basin being: (1) permanent (or seasonal) inputs of terrestrial material that supply organic matter, Fe and Mn oxides and elements associated with, (2) pronounced trapping effect under restricted water exchange with an open sea, (3) contrast oxidizing conditions within the water column and upper sediments, that influence the element cycling and speciation and, hence, may increase potential contaminant bioavailability and toxity. Therefore, it is essential to know more about the carriers and transport modes of potential contaminants such as trace heavy metals and their response to the specific biogeochemical conditions of separating basins. The objective environmental assessment of such ecosystems requires comprehensive biogeochemical examination, while the complex characterization of sediments from such unstable environments can serve as a basis of ecological monitoring 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.

The present chapter continues and summarizes the series of ecological researches of the White Sea restricted exchange environments. Hence, in this work the TOC, *n*-alkanes and metal (Fe, Mn, Cu, Zn, Cr and Pb) forms distribution in surface sediment samples from representative small exchange environments of the Karelian shore being Kislosladkoe Lake, Cape Zeleny Lake, Chernorechenskaya Bay and Porchalische Lagoon was determined and discussed in relation to the hydrological and hydrochemical features of representative basins. Since major and trace element speciation is essential in processes such as the toxity

and bioavailability of pollutants in natural systems, the special goal of the study is the comparative study of ecologically significant metal forms in sediments of separating basins.

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 90000 km^2, with a water volume of some 6000 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 km^3 per year (Dobrovolsky & 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 fresh-water 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. 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
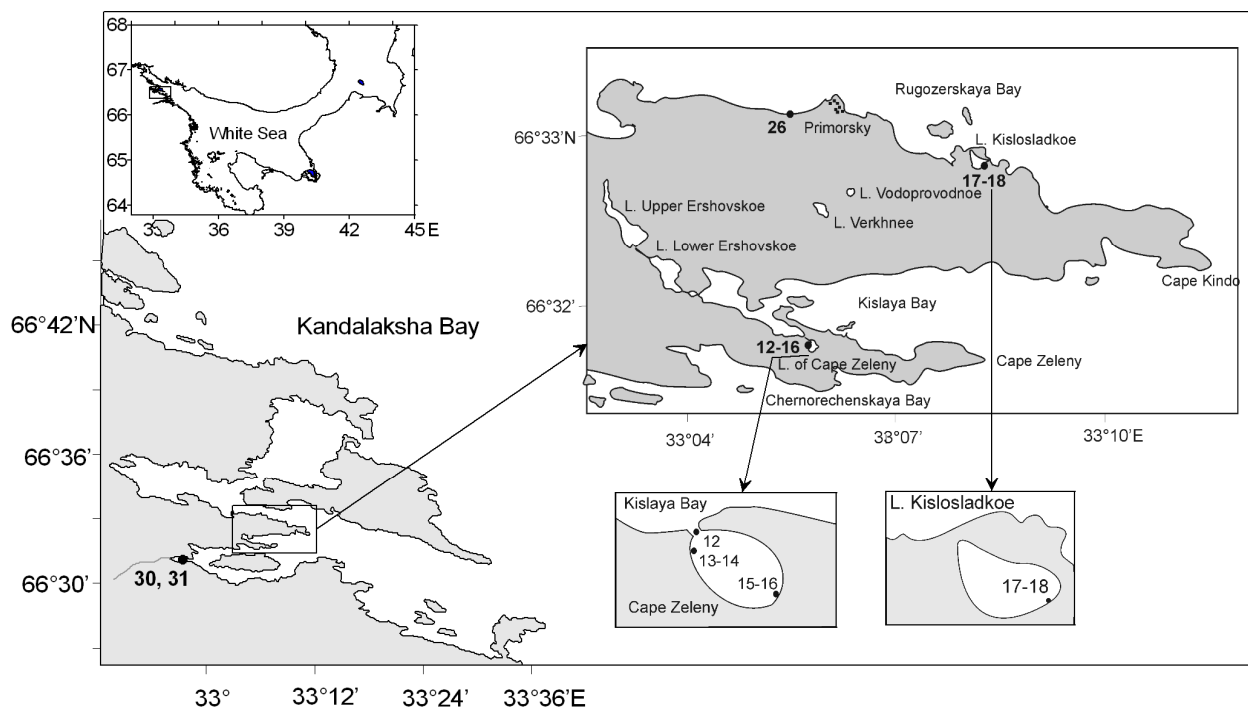

Fig. 1. Map of Kandalaksha Bay of the White Sea showing the location of the sampling stations.

severely restricted. The present study focuses on four small basins along the Karelian shore of Kandalaksha Bay, in the vicinity of the White Sea Biological Station of Moscow state Lomonosov University: Chernorechenskaya Bay (the inner part), Kislosladkoe Lake, Cape Zeleny Lake, and Porchalische lagoon (Fig. 1).

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 between the 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.

Porchalische lagoon is a littoral pool located 300 m to the north from Primorsky village 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 28.08-10.09.2008 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 & 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.

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 hours. 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 hours. 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 1M 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 Moscow State Lomonosov University. The relative accuracy for AAS determinations was within the standard deviations of the certified sediment reference material SDO-1 (Berkovitz & Lukashin, 1984).

3. Results and discussion

3.1 Water column

The water column structure discussion is based on the research of Cape Zeleny Lake and Kislosladkoe Lake by Shaporenko S.I. and co-authors (Shaporenko et al, 2005). The specific conditions of shallow separating basins being restricted water exchange with an open sea, permanent fresh water input and bottom relief complicated by depressions lead to extreme values of hydrological and hydrochemical parameters within the water column during the

summer period (Fig. 2). The hydrological and hydrochemical stratification of the water column strongly differs from the open coastal White Sea. The most specific features are: thin surface fresh water layer, sharp halocline, high temperature and extreme high oxygen concentrations (more than 20 mg/l that makes up to 300% of saturation capacity) in subsurface water layer, while low temperature and extreme high H_2S concentrations (more than 90 mg/l) in the bottom depressions. The active water reaction (pH) in the upper aerobic layers of the lakes was slightly alkaline (8-9), near the oxic-anoxic layers boundary and in the anaerobic near bottom layer – close to neutral (7-7.5). The water alkalinity in the lakes varied within the ranges of 40 to 70 mg $CaCO_3$ per 1 liter, while its distribution followed that of salinity. The CO_2 concentration in the lakes waters increased from surface (9-11 mg/l) to the bottom layer (up to 400 mg/l). The phosphorus forms contents in the waters of the lakes did not exceed the respective averaged values for Kandalaksha Bay. However, the lakes waters were enriched in all nitrogen forms in comparison to the open White Sea, while NH_4^+ concentration was especially enhanced probably due to the anaerobic zones occurrence. The total dissolved iron varied within the ranges 0.01-0.03 mg/l and was found twice orders higher the background values.
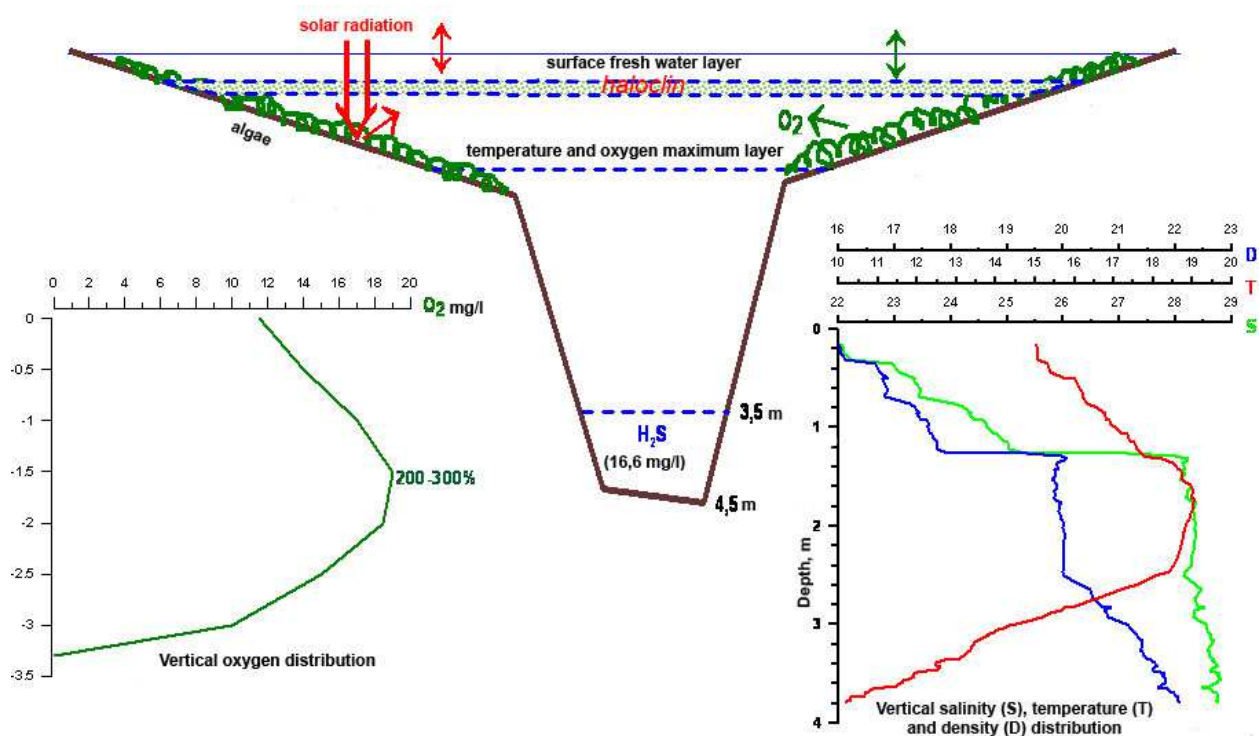

Fig. 2. Water column structure of typical separating basin (Kislo-Sladkoe lake, summer 2001; Shaporenko et al, 2005)

The thin fresh water layer is separated from the temperature and oxygen maximum layer by the sharp halocline. The halocline provides the vertical sustainability of the water stratification and preserves the lower layers from mixing. In shallow waters, under sufficient light and heat, the active growth of thread algae occurs. The algae may cover up to 80-90% of shallow lake bottom. The intensive photosynthesis at the algae extent causes the permanent input of O_2 into the water column. Since the salinity and density cline preserves

the water layers from mixing, the oxygen is not released to the surface water layer contacting the atmosphere – and is therefore accumulated within the subsurface waters forming the oxygen maximum layer. In the bottom depressions, on the contrary, the poor water mixing and intensive organic matter accumulation and decomposition cause the extensive sulfate reduction and elevated H_2S concentration in the near bottom waters. Thus, within the water column the sharp change from oxic to redox conditions is observed. The absence of sharp density gradient between oxygen and hydrosulfuric zones is a specific feature of the Karelian shore separating basins. Hence, the upper aerobic waters here are relatively enriched in NH_4^+ and CO_2, and other biogenous elements.

During the seasons with low photosynthesis, the hydrosulfuric zone may spread towards the water surface up to the halocline. Moreover, in winters, under the ice cover, the anaerobic conditions may occur in the whole water column. Due to this, the resident species within the ecosystem are stressed and the regular mass biota extinctions occur.

3.2 Sediment distribution and biogeochemical characteristics

3.2.1 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 the 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 transported by ice. The heavy mineral fraction of quartzo-feldspathic sand-size material is mainly comprised of pyroxene, epidote, garnet, and hornblende. The major clay minerals of the fine-grained fraction are illite (50-80%) and chlorite (20-30%), with an admixture of montmorillonite and kaolinite (Pavlidis, 1995). Most of the source material was originally derived from the Archean igneous (widely ranged from ultrabasic to persilic and from normal to alkaline row) and metamorphic (mostly gneisses, crystalline schists, amphibolites) rocks that form the White Sea geological block of the Baltic Shield (Milanovsky, 1987). In addition, a few appearances of Paleozoic ultrabasic alkaline dike were found at the Rugozerskaya site in the vicinity of the White Sea Biological Station of Moscow State University (Shurkin, 1984). Sediments derive from the submarine erosion of rock outcrops, the reworking of old glacial deposites during post-glacial sea-level rises, glacial outwash, and ice-rafting.

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). 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, 2003).

The physical and chemical environments of estuarine and coastal sediments and within the Karelian coastline, in particular, vary over wide ranges. Sediments underlying oxic bottom waters, have layered structure. The upper centimeters of such usually muddy impermeable sediments have an oxic "cap" just below the sediment-water interface, where Fe and Mn oxides precipitate; below the oxic layer is a region of Fe and S reduction, but without buildup of dissolved H_2S. 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 both form insoluble sulfides and tend to sorb on to precipitating Fe and Mn oxides. Hence, they are released to pore waters when Fe and Mn oxide reduction occurs, but tend to be immobilized by precipitation as sulfides. In sediments, underlying permanently or seasonally anoxic bottom water, hydrosulfuric layer is spread to the sediment-water interface providing the free upward transport of reduced Fe, Mn and S from sediments to near bottom waters. Thus, the dissolved H_2S, Fe and Mn exhibited sharp content maximums in the near bottom anaerobic water layers of lakes Kislosladkoe and Cape Zeleny (Shaporenko et al, 2005). The other important coastal sediment type is permeable sandy sediment, in which the aerobic conditions usually prevail but element accumulation hardly occurs due to the low adsorption capacity of sand material. Most of the sediments studied from Kislosladkoe, Cape Zeleny and Chernorechenskaya underlie the oxic waters and, therefore, have the oxic cap on top 1-3 cm. In these muddy samples, the oxic cap and the underlying sediment were sampled and analyzed separately (st. 13-14, 15-16, 17-18, 30-31). Hydrosulfuric sediment from Porchalische lagoon (st. 26) and silty sand from the stream bed of Cape Zeleny Lake (st. 12) had no visible layers.

3.2.2 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). The most found values of organic carbon are within the range of average marine and Arctic Ocean sediments (Romankevich, 1984).

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
Cherno-rechenskaya 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 1. TOC, carbonates and n-alkanes distribution in surface sediments.

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 that is characteristic for surface oxic sediment layer (Romankevich & Vetrov, 2001). At the same time, in high-energy areas (such as estuarine water mixing zones) the effects of sediment resuspension can dominate sediment-water-column exchange (Postma, 1980). Thus, 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 moderate 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. The fine-grained silt from Porchalische was characterized by a noticeable hydrosulfuric smell and the absence of the yellowish oxic layer that is typical of sediments underlying the anoxic bottom waters and experiencing the high flux of organic matter. The marine algae brought into the lagoon by storms cannot survive under the stress from regular tidal sea-fresh water change (Vetrov & Peresypkin, 2009). Further deposition and decomposition of the algal mass might contribute to an increased accumulation rate of organic matter and hence to 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.

3.2.3 *n*-alkanes distribution

The total *n*-alkanes content ranged from 0.2 µg g^{-1} to 7.4 µg g^{-1} (mean 3.3 µg g^{-1}) (Table 1). These values are considered to be relatively low for the area studied (Peresypkin & 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.3) 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 especially pronounced in the Porchalische lagoon (st. 26).
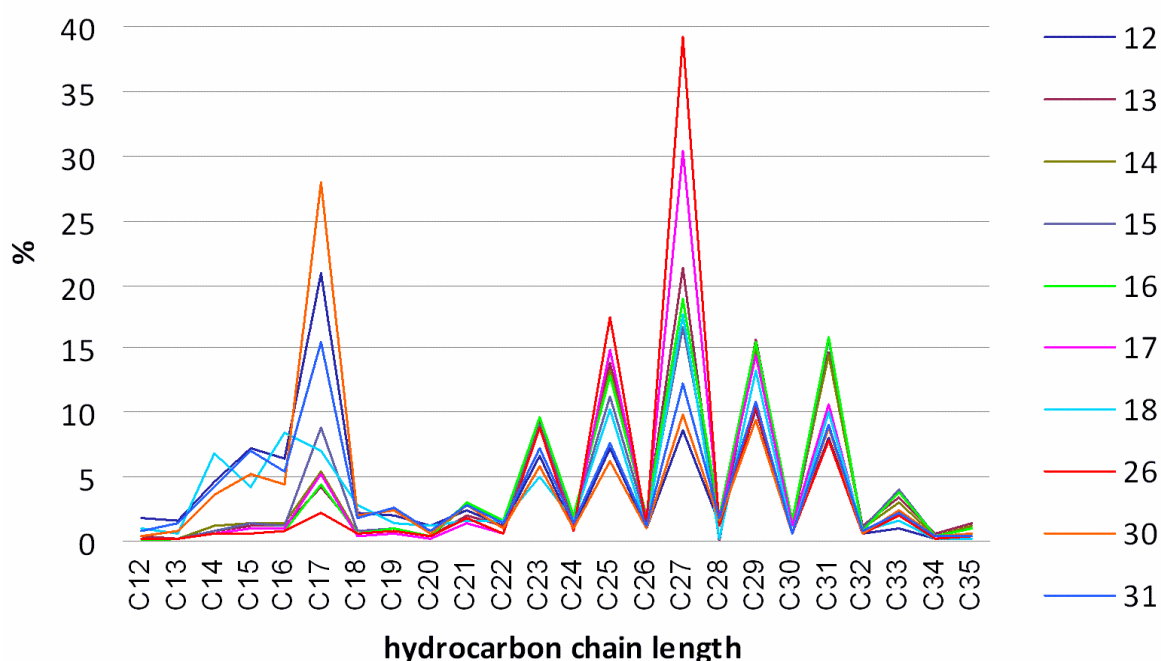

Fig. 3. The distribution of *n*-alkanes in surface sediments.

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 µg 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 & Belyaev, 2009, Vetrov & Peresypkin, 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.

Thus, the found TOC and *n*-alkanes distribution showed that sediments from studied basins tend to be terrigenous with major input of organic matter from terrestrial plant remains. The transformation of the original organic matter in sediments studied often occurs under redox conditions. The minor presence of autochthonous microbial sources may indicate the microbial community extension.

3.3 Metals in sediments

3.3.1 Abundance and distribution of metals in surface sediments

Trace heavy metals enter coastal environments with a terrigenous fresh water discharge from the drainage area, with the precipitates and aerosols. Within the water column, dissolved metal forms are actively adsorbed on to suspended particulate matter (SPM). Further sedimentation of suspended particles contributes to trace heavy metal accumulation within the sediment phase (Foerstner & Wittmann, 1981). Within the sea-fresh waters barrier zone, flocculation and coagulation of the dissolved (colloidal) and fine suspended matter (such as clay particles, oxyhydroxides and organic substances) initiated at the salinity gradient lead to metal enrichment of the deposited material, since the dissolved and particulate metals are actively incorporated in (sorbing on) newly formed aggregates (Morris, 1986). Although, some dissolved metal entering the aquatic environments may be directly fixed by bottom sediments "escaping" the SPM phase (Dauvalter, 1998a). Therefore, bottom sediments being a long-term natural element "traps" may be used as preferential indicators of the trace heavy metals environmental pollution degree.

Anthropogenic materials (e.g. trace heavy metals) can both be present in the sediments from deposition in the past and can arrive with current deposits, while sediment resuspension and subsequent reaction and transport in the water column can be an important mechanism for redistribution of trace contaminant metal. Within the Karelian coastline, the small-scale geochemical patterns and disparities complicate the assessment of natural geochemical background of the region under investigation (Koukina et al, 2003). Therefore, the found mean trace heavy metal content values were compared with those found in previous studies for surface sediments from the other White Sea regions, where the anthropogenic trace heavy metal contamination was not detected. These systems are: the Karelian shore small bays (Ermolinskaya, Griaznaya, Poyakonda, Podvolochie, Chernorechenskaya), Chupa estuary (Chupa Bay of Kandalaksha Bay) and Dvina Bay of the White Sea (Table 2). To assess the ecological status of the Karelian shore sediments, the found content values were also related to the available sediment quality guidelines for trace heavy metals.

The mean contents of Pb, Cu, Zn and Cr in Karelian shore separating basins are comparable or lower the respective values from other Kandalaksha Bay regions and Dvina Bay of the White Sea. According to effects range-low (ERL) and effects range-median (ERM) sediment quality guidelines for trace metals, all found contents for Karelian shore separating basins were below both the ERL and ERM levels generally suggested to have potential adverse biological effects of 20-30% and 60-90% of incidence, respectively (Long et al, 1995). Hence, the sediments studied were related to uncontaminated by trace heavy metals and by Pb, Cu, Zn and Cr, in particular.

	n	Pb	Cu	Zn	Cr	Source
Karelian shore separating basins	10 SD	4 2	16 12	118 70	41 18	Present study
Karelian shore small bays	18 SD	16 8	16 11	141 26	169 46	(Koukina et al 2003)
Chupa Bay*	11 Range	21 12-25	18 15-22	85 57-110	nd nd	(Millward et al 1999**)
Dvina Bay	13 SD	20 14	21 8	76 27	84 26	(Koukina et al 2001)
ERL guideline value	Incidence of adverse effect 20-30%	47	34	150	81	(Long et al, 1995)
ERM guideline value	Incidence of adverse effect 60-90%	218	270	410	370	(Long et al, 1995)

Table 2. Mean metal contents ($\mu g\ g^{-1}$) in the surficial sediments from the Karelian shore separating basins, Karelian shore small bays, Chupa estuary, Dvina Bay, effects range-low (ERL) and effects range-median (ERM) sediment quality guidelines values for trace metals; n - number of samples, SD – standard deviation to nearest $\mu g\ g^{-1}$, * - range of contents for <63 μm sediment fraction, ** - as cited in Koukina et al, 2003.

St.	Pb_{tot}	Cu_{ac}	Cu_{alk}	Cu_{tot}	Zn_{ac}	Zn_{alk}	Zn_{tot}	Cr_{ac}	Cr_{alk}	Cr_{tot}	Mn_{ac}	Mn_{alk}	Mn_{tot}	Fe_{ac}	Fe_{alk}	Fe_{tot}
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	22710
14	1	2	1	13	5	4	151	1	<0.5	50	4	<0.5	115	594	509	17400
15	6	1	1	8	6	4	31	3	2	49	5	2	88	1504	1595	19240
16	6	1	<0.5	13	7	4	61	2	1	52	4	1	106	1900	1710	20500
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	12890
30	5	1	1	12	5	4	128	1	<0.5	45	5	1	80	775	418	16100
31	5	1	1	12	5	3	128	2	1	51	25	19	102	3030	2390	20500
m	4	1	1	16	6	6	118	1	1	41	7	3	85	968	936	14664

Table 3. Acid soluble (labile, Me_{ac}), alkali soluble (organically bound, Me_{alk}) and total metal (Me_{tot}) distribution in surface sediments ($\mu g\ g^{-1}$).

Trace metal distribution in coastal sediments depends on the sediment type and major elements – the carriers (TOC, Fe, Mn) abundance (Koukina et al, 2002, 2010). Table 3 shows the total metal and metal forms contents in the Karelian shore sediments, while table 4 shows the Spearman correlations between elements studied. Among elements studied, Fe is major element and 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 $\mu g\ g^{-1}$, and total Cr ranged from 11 to 68 $\mu g\ g^{-1}$, while Mn and Cr distribution was similar to that of Fe (Spearman correlation coefficient r_s was 0.92 and 0.98, respectively, Table 4). 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 3, 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 and Fe-Mn bearing minerals mobilized from adjacent soils, stream and river beds, and ground waters. 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 positively correlated with TOC (r_s=0.57) and had a clear content maximum in the organic rich sediment from Porchalische lagoon (59 µg g-1). Total Zn showed no pronounced affinity to major and trace elements studied but exhibited sporadic sharp enrichments (160-240 µg g-1) in some sediments of Cape Zeleny Lake (st.12, 14, 16), Kislosladkoe Lake (st. 18) and organic rich sediment of the Porchalische lagoon (st. 26).

The vertical metal distribution within the upper sediment column is influenced by the oxidation-reduction reactions and authigenic mineral formation (Dauvalter, 1997, Moiseenko et al, 2009a). At most of the sites, where the muddy sediments underlie the oxic bottom water, the top oxic layer was enriched in Fe, Mn, Cr and, in a lesser extent, in Cu and Pb. Increased contents of Fe, Mn and elements associated with in the top oxic sediment layer are due to the precipitation and accumulation of Fe and Mn oxides at the sediment-water interface. Fe and Mn may be also supplied to the top layer in the reduced dissolved forms, which diffuse from the lower layers of sediment column where Fe and SO_4 reduction under anaerobic conditions occurs. 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 top oxic layer (st. 15-16, 30-31). In the layer of Fe and S reduction and below, sulfates in sediments are reduced to form of hydrogen sulfide. The newly formed hydrogen sulfide is bound by mobile forms of ferrous oxide to monosulfide and, in the same time, experiences bacterial transformation into free sulfur. In this form, sulfur and the lower metal oxides form such minerals as pyrite, chalcopyrite, pentlandite, covellite etc (Dauvalter, 1998b, Dauvalter, 2000, Moiseenko et al, 2009b). Thus, the post-depositional diagenetic effects of Fe-Mn cycling both at and near the sediment-water interface may lead to subsurface metal accumulation (Loring et al, 1998).

In the most of the samples with an oxic cap, subsurface sediments exhibited at least twice higher Zn content comparing to the surface oxic layer. These are sediments from Cape Zeleny Lake (st. 13-14, Zn content 60-150 µg g-1 , st. 15-16, Zn 30-60 µg g-1) and especially Kislosladkoe Lake (st. 17-18, Zn 30-240 µg g-1). According to the vertical structure of these sediments, below the oxic cap (in the anaerobic layer) FeS and other metal insoluble sulfides may be formed due to the precipitation of Fe (III) and SO_4^{2-} reduction products. The presence of sulfides is considered to be one of the major factors controlling the immobilization of metals in sediments, since most of divalent metals form insoluble sulfides or coprecipitate and adsorb on to iron sulfides. Thus, divalent Zn is shown to be bound by reduced S forming sphalerite ZnS in the flooded soils and lake sediments. Moreover, under anaerobic conditions Zn^{2+} may be coordinated by reduced S-containing functional groups of humic substances (Vodianitzky, 2008, 2009). Thus, under anaerobic conditions Zn may form insoluble sulfides and complexes with organic substances that may cause Zn subsurface content maximums. The abundance and 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. Heavy minerals, enriched in microelements, are always present in the dust fraction of soils and terrigenous sediments that originate from the bedrocks of respective biogeochemical province (Motuzova, 2009). Thus, Zn as a chalcophile element may preferentially concentrate in some of the rock-building minerals, characteristic for Karelian shore, for example, ferromagnesium silicates. Indeed, some hornblendes and pyroxenes of alkaline rocks characteristic for the area may contain up to 600 g tonne $^{-1}$ of Zn (Ivanov et al, 1973, Ivanov, 1997).

Therefore, the Spearman correlation analysis and metal distribution in relation to oxic-anoxic boundary within the upper centimeters of sediment column revealed following element associations. Fe, Mn, Cr and, in a lesser extent, Pb preferentially accumulate within the top oxic layer due to the precipitation with Fe-oxyhydroxides. Cu also tends to accumulate in surface sediments, but its sedimentation is to a higher degree bound to organic matter sedimentation processes than for other metals studied (Koukina et al, 1999, 2001, 2010). Zn enrichments in the subsurface zone are most likely controlled by a sulfide-associated phase.

	Cu_{ac}	Cu_{alk}	Cu_{tot}	Zn_{ac}	Zn_{alk}	Zn_{tot}	Pb_{tot}	Cr_{ac}	Cr_{alk}	Cr_{tot}	Mn_{tot}	Fe_{ac}	Fe_{alk}	Fe_{tot}	TOC
Cu_{ac}	1,00	**0,68**	**0,70**	0,36	**0,80**	-0,07	-0,25	-0,03	-0,01	0,23	0,40	-0,09	-0,11	0,17	0,35
Cu_{alk}	**0,68**	1,00	0,54	0,47	**0,85**	-0,10	-0,23	-0,26	-0,09	-0,23	-0,18	-0,30	-0,08	-0,19	0,62
Cu_{tot}	**0,70**	0,54	1,00	**0,73**	**0,74**	-0,16	-0,05	0,03	0,17	0,44	0,48	0,11	0,32	0,38	0,57
Zn_{ac}	0,36	0,47	**0,73**	1,00	0,57	-0,45	0,02	0,06	0,42	0,21	0,20	0,20	0,46	0,21	**0,82**
Zn_{alk}	**0,80**	**0,85**	**0,74**	0,57	1,00	-0,04	-0,31	-0,36	-0,11	-0,07	0,01	-0,28	-0,08	-0,12	**0,63**
Zn_{tot}	-0,07	-0,10	-0,16	-0,45	-0,04	1,00	-0,60	**-0,75**	**-0,96**	-0,47	-0,41	-0,57	**-0,72**	-0,53	-0,44
Pb_{tot}	-0,25	-0,23	-0,05	0,02	-0,31	-0,60	1,00	**0,68**	**0,70**	0,62	0,46	0,60	0,49	**0,69**	-0,04
Cr_{ac}	-0,03	-0,26	0,03	0,06	-0,36	**-0,75**	0,68	1,00	**0,86**	**0,76**	**0,72**	**0,74**	**0,72**	**0,82**	0,04
Cr_{alk}	-0,01	-0,09	0,17	0,42	-0,11	**-0,96**	0,70	0,86	1,00	**0,64**	0,57	**0,67**	**0,78**	**0,69**	0,37
Cr_{tot}	0,23	-0,23	0,44	0,21	-0,07	-0,47	0,62	**0,76**	**0,64**	1,00	**0,96**	**0,79**	**0,66**	**0,98**	0,05
Mn_{tot}	0,40	-0,18	0,48	0,20	0,01	-0,41	0,46	**0,72**	0,57	**0,96**	1,00	**0,68**	0,53	**0,92**	0,03
Fe_{ac}	-0,09	-0,30	0,11	0,20	-0,28	-0,57	0,60	**0,74**	**0,67**	**0,79**	**0,68**	1,00	**0,79**	**0,84**	0,03
Fe_{alk}	-0,11	-0,08	0,32	0,46	-0,08	**-0,72**	0,49	**0,72**	**0,78**	**0,66**	0,53	**0,79**	1,00	**0,72**	0,44
Fe_{tot}	0,17	-0,19	0,38	0,21	-0,12	-0,53	**0,69**	**0,82**	**0,69**	**0,98**	**0,92**	**0,84**	**0,72**	1,00	0,08
TOC	0,35	0,62	0,57	**0,82**	**0,63**	-0,44	-0,04	0,04	0,37	0,05	0,03	0,03	0,44	0,08	1,00

Table 4. Spearman rank order correlation matrix for acid soluble (Me_{ac}), alkali soluble (Me_{alk}) and total (Me_{tot}) metals and TOC in surface sediments, (n=10, marked correlations are significant at p<0.05).

3.3.2 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 & 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 (Gerson et al, 2008, Krishnamurti, 2008). 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 & 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. Metals in mineral form cannot be easily recycled into the water column due to a higher vulnerability of mineral components to post-depositional diagenetic processes.

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 & Rantala, 1992). The proportion of the total metal removed by the extraction is defined as acid soluble (non-detrital) metal fraction in sediments. The 0.1M 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. 0.1M sodium pyrophosphate is known to mobilize also some part of easily soluble amorphous Fe-oxides and hence the elements associated with (Vorobyova, 2006).
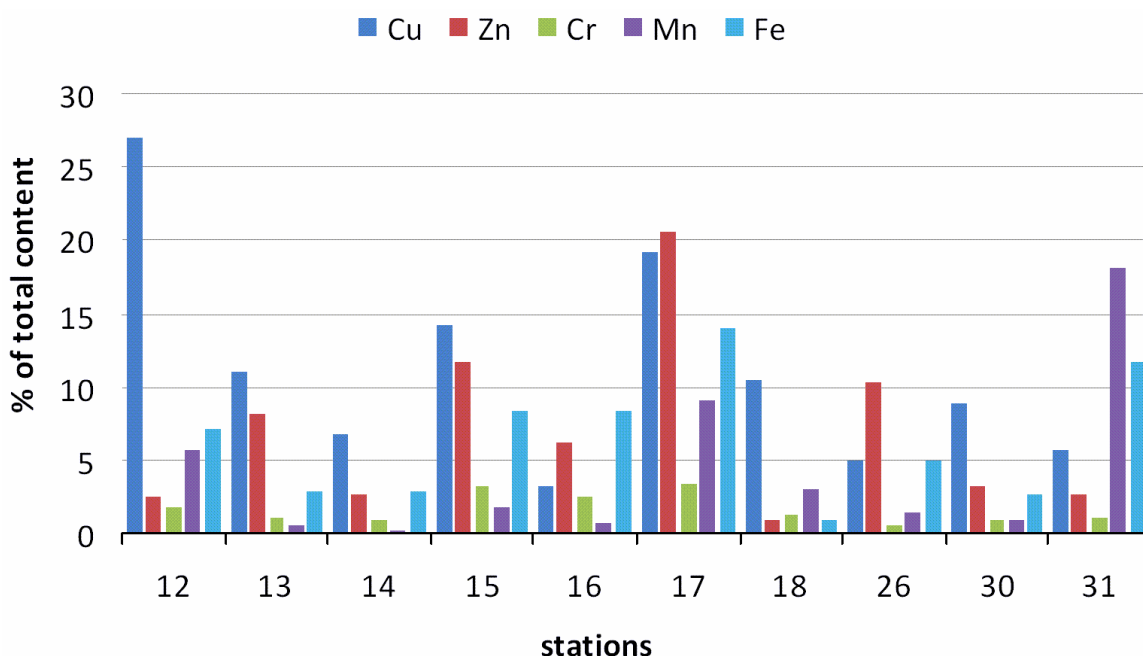

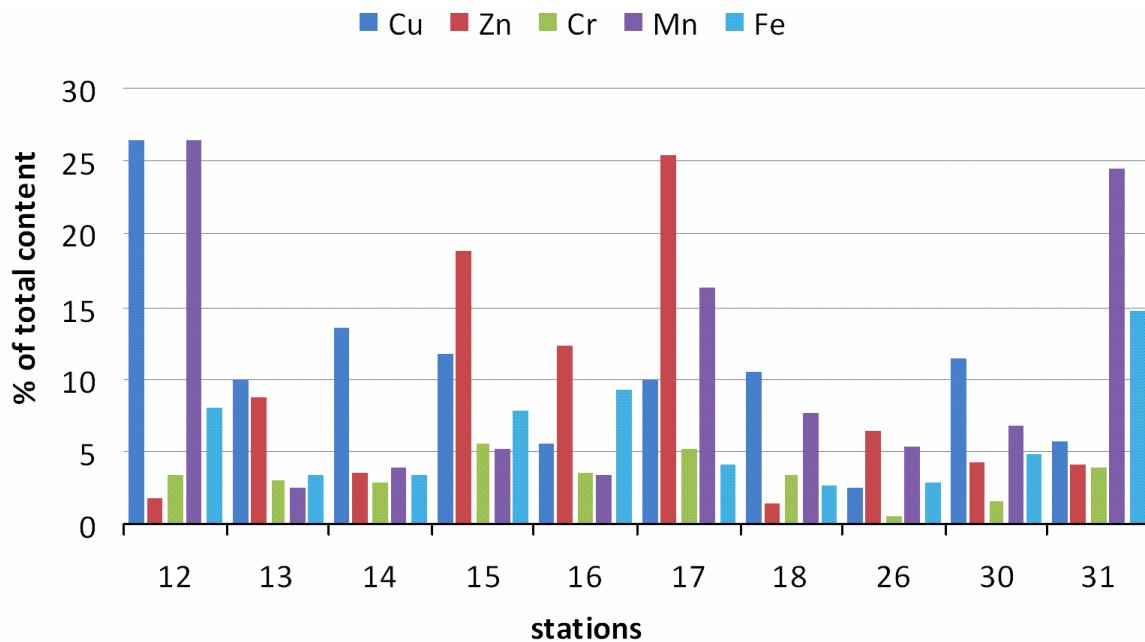Fig. 4. The distribution of acid soluble (labile) metals in surface sediments.

Fig. 5. The distribution of alkali soluble (organically bound) metals in surface sediments.

The amounts of metals extracted by 25% acetic acid and 0.1M 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 µg g⁻¹ for Fe, 3-25 µg g⁻¹ for Mn, 1-3 µg g⁻¹ for Cr, 1-2 µg g⁻¹ for Cu, and 3-12 µg 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 µgg⁻¹ for Fe, 1-19 µg g⁻¹ for Mn, 1-2 µg g⁻¹ for Cr, 1-3 µg g⁻¹ for Cu, and 2-19 µg 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). 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.

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, Table 4), 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 correlations with other elements studied (therefore these correlations were excluded from table 4). 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). 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 (Fig. 3 and 4). Mn is known to be precipitated from solution at pH>8, while the 0.1M sodium pyrophosphate has pH 10, at which the labile Mn and associated elements might be immobilized (Vodianitzky, 2009). 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. Therefore, in sediments studied the most bioavailable metal fraction is mostly comprised of metals held in ion exchange positions, weakly bound to organic matter and, in a greater extent, associated with easily soluble amorphous Fe-oxides, abundant in terrigenous sediments. Organic matter starts to play a critical role in concentration metals via ligand binding at the sufficient TOC content of organic rich sediments. Among elements studied the most bioavailable part of Zn and Cu is probably bound to organic substances, while bioavailable Cr and Mn are in a greater extent controlled by Fe-oxyhydroxide formation.

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 by the *n*-alkanes distribution study. Hence, the role of microbial community in element speciation in sediments needs special study. 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.

Taking into account the individual metal affinity to organically bound or labile fraction, an average, the 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 to some extent due to a crossing 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. However, the found amounts of labile and organically bound metal forms in studied separating basins exceeded the respective values of labile metal fraction for sediments from previously studied open small bays of the Karelian shore (that made up an average only 2-5% of total metal content) and corresponds to the enhanced labile metal (6-8 % for Fe, Mn, Zn, Cr) contents found in separating lagoons of Chernorechenskaya Bay (Koukina et al, 2010). Major and trace elements entering the separating basins with fresh water discharge are scavenged by Fe-Mn oxides and bound to coagulating organic substances in the course of sedimentation processes, with further burial in surface sediments in labile forms. The anaerobic conditions in the bottom depressions and their winter extension within the water column cause the release of labile metals to pore and bottom waters. While some trace metals may be immobilized by precipitation as sulfides at sufficient H_2S concentration, regular change of oxidizing conditions at permanent element input from fresh water supply contributes to relative accumulation of bioavailable metal forms in sediments. Hence, at the found low or close to background trace heavy metal

contents, in separating basins the relative part of labile bioavailable metals is still enhanced in relation to the neighboring open coastal sea.

4. Conclusion

Restricted exchange environments studied varied from typical small estuary Chernorechenskaya, complicated by shallow bars, to separating basins of different isolation stage being Cape Zeleny Lake and Kislosladkoe Lake, and to the isolated littoral pool - Porchalische lagoon. The specific conditions of separating basins under investigation being restricted water exchange with open sea, permanent or seasonal fresh water input and bottom relief complicated by depressions lead to extreme values of hydrochemical parameters during the summer period, while the most specific features are contrast oxidizing conditions within the water column with anoxia zones occurrence in the bottom depressions that may be spread on to the whole water body in winters. The evolution of sediments here is strongly affected by small-scale variability in oxidizing conditions.

The found TOC and *n*-alkanes distribution showed that sediments from studied basins tend to be terrigenous with major input of organic matter from terrestrial plant remains. The transformation of the original organic matter in sediments studied often occurs under redox conditions which are especially pronounced in the Porchalische lagoon. The revealed presence of autochthonous microbial sources of the organic matter in sediments may indicate the microbial community extension within the ecosystems.

The total trace heavy metal contents in sediments from separating basins studied corresponded to the respective values for other White Sea regions uncontaminated by trace heavy metals and were below the threshold levels according to sediment quality guidelines. Hence, in the restricted exchange environments studied no significant contamination by trace heavy metals (Pb, Cu, Zn and Cr, in particular) was detected. Spearman correlation analysis and total metal distribution in relation to oxic-anoxic boundary within the upper centimeters of sediment column revealed element affinity to different sediment components. Thus, Fe, Mn, Cr and, in a lesser extent, Pb preferentially accumulate within the top oxic layer due to the precipitation with Fe-oxyhydroxides. Total Cu also tends to accumulate in surface sediments, but its sedimentation is to a higher degree bound to organic matter sedimentation processes than for other metals studied. Total Zn enrichments in the subsurface zone are most likely controlled by a sulfide-associated phase and/or bound to Zn-rich detrital minerals.

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. Therefore, the most bioavailable part of metals is comprised of metals held in ion exchange positions, weakly bound to organic matter and, in a greater extent, associated with easily soluble amorphous Fe-oxides, abundant in terrigenous sediments. Organic matter starts to play a critical role in concentration of metals at the sufficient TOC content of organic rich sediments. The found amounts of labile and organically bound metal forms exceeded the respective values for previously studied small bays of the Karelian shore. Hence, in separating basins the relative part of labile bioavailable metals is enhanced in relation to the neighboring open coastal sea. In separating basins, the

regular change of oxic to anoxic conditions in sediments and waters by permanent element input from fresh water supply contributes to relative accumulation of bioavailable metal forms in sediments.

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. Major and trace elements entering the separating basins with fresh water discharge are scavenged by newly forming Fe-Mn oxides and bound to coagulating organic substances in the course of sedimentation processes, with further burial in surface sediments in potentially bioavailable labile forms that can be further recycled to water column. Among elements studied the most bioavailable part of Zn and Cu is probably bound to organic substances, while bioavailable Cr and Mn are in a greater extent controlled by Fe-oxyhydroxide formation. According to their averaged potential bioavailability, the elements studied may be arranged in the following decreasing sequence: Cu>Zn>Mn>Fe>Cr.

The present study is essential for the prognosis of Arctic ecosystems vulnerability and, in particular, anoxia occurrences in Arctic coastal environments. The most vivid example is the Porchalische lagoon, where at highest (among sites studied) organic matter accumulation rate the anoxic sediments exhibited the enhanced contents of potentially bioavailable trace heavy metals. Such ecologically unfavorable situation might be typical for central bottom depressions of separating basins in summer and may be aggravated in winter periods.

5. Acknowledgment

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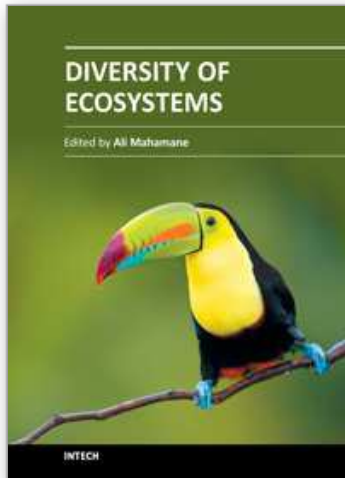
Diversity of Ecosystems

Edited by Prof. Mahamane Ali

The ecosystems present a great diversity worldwide and use various functionalities according to ecologic regions. In this new context of variability and climatic changes, these ecosystems undergo notable modifications amplified by domestic uses of which it was subjected to. Indeed the ecosystems render diverse services to humanity from their composition and structure but the tolerable levels are unknown. The preservation of these ecosystemic services needs a clear understanding of their complexity. The role of research is not only to characterise the ecosystems but also to clearly define the tolerable usage levels. Their characterisation proves to be important not only for the local populations that use it but also for the conservation of biodiversity. Hence, the measurement, management and protection of ecosystems need innovative and diverse methods. For all these reasons, the aim of this book is to bring out a general view on the function of ecosystems, modelling, sampling strategies, invading species, the response of organisms to modifications, the carbon dynamics, the mathematical models and theories that can be applied in diverse conditions.

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