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METAL FORMS IN SEDIMENTS FROM SEPARATING BASINS OF THE KARELIAN SHORE (KANDALAKSHA BAY, WHITE SEA, RUSSIAN ARCTIC).

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The present study continues the series of environmental researches of the White Sea restricted exchange environments. In this work, the TOC

and metals (Fe, Mn, Cu, Zn, Cr and Pb) distribution in surface sediment samples from Kislosladkoe Lake, Zeleny Mis Lake and small separating lagoons of the Karelian shore was determined and discussed in relation to the hydrological and hydrochemical features of the basins that were studied. 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 research is the comparative study of ecologically significant metal forms in sediments.

The specific conditions of the shallow separating basins of the White Sea include contrasting oxidising conditions within the water column and the occurrence of anoxia zones in the bottom depressions that may spread throughout the water body during the winter. The maturation of the sediments is strongly affected by small-scale variability in their physical and chemical conditions.

The observed trace heavy metal contents in the sediments from the separating basins were comparable to corresponding values for other White Sea regions that are uncontaminated by trace heavy metals and were below the threshold levels according to sediment quality guidelines (Table 1). Therefore, in the restricted exchange environments that were studied, no significant contamination by trace heavy metals (Pb, Cu, Zn and Cr, in particular) was detected. The total metal distribution in relation to the oxic-anoxic boundary within the upper few centimetres of the sediment column revealed elemental affinity toward different sediment components. Fe, Mn, Cr and, to a lesser extent, Pb preferentially accumulate within the top oxic layer due to precipitation with Fe-oxyhydroxides. Accumulation of Cu in the surface oxic sediments is controlled to a greater extent by organic matter sedimentation processes. The observed Zn enrichments in the anoxic subsurface zone are most likely controlled by a sulphide-associated phase (Table 2).

The comparative study of the two most bioavailable metal forms that were labile (acid soluble) and organically bound (alkali soluble) showed that acetic acid and sodium pyrophosphate released comparable amounts of metals from the sediments, i.e. 3–11% and 2–12% of the total metal content, respectively. The most bioavailable parts of metals are weakly bound to organic matter and, to a greater extent, associated with easily soluble amorphous Fe-oxides that are abundant in terrigenous sediments. Organic matter starts to play a critical role in the concentration of metals via ligand binding in organic rich sediments (TOC ≥ 5%). Among the elements that were studied, the most bioavailable part of Zn and Cu was most likely bound to organic substances,

whereas bioavailable Cr and Mn were controlled to a greater extent by the formation of Fe-oxyhydroxides.

Table 1. Mean metal contents (μg 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 μg g^{-1}, * — range of contents for <63 μm sediment fraction.

	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)

The elements studied can be arranged in the following decreasing order of average potential bioavailability: Cu>Zn>Mn>Fe>Cr>Pb. Among the sites studied, the elevated contents of bioavailable metal forms are related to sediments that are enriched in organic matter and/or located within sea waterfresh water barrier zones.

The observed amounts of labile and organically bound metal forms exceeded corresponding values for previously studied small bays of the Karelian shore (Table 3). Therefore, in the separating basins, the rela-

tive proportion of labile bioavailable metals is enhanced in relation to the neighbouring open coastal sea, possibly due to the spread of anoxic conditions across sediments and water levels. Thus, under separation processes, sediments exhibit enhanced contents of bioavailable trace heavy metals.

Table 2. Metal partition in surface sediments.

Elements	Fe, Mn, Cr, Pb	Cu, TOC	Zn
Sediment layer	top oxic (0–1–3 cm)	top oxic (0–1–3 cm)	subsurface anoxic (1–3–6 cm)
Phase / process	co-precipitation with Fe-Mn oxyhydroxides	specific adsorption by organic matter via ligand binding	insoluble sulfide formation

Table 3. Bioavailable metal forms in surface sediments.

Extraction	Major metal fraction extracted	Basin	Elements	% of total metal content	Source
25% CH_3COOH	bound to amorphous Fe/Mn compounds	open bays	Fe, Mn, Cu, Zn, Cr, Pb	2–5%	Koukina et al, 2010
		separating basins	Fe, Mn, Cu, Zn, Cr	3–11%	present study
0.1 M $Na_4P_2O_7$	organically bound	separating basins	Fe, Mn, Cu, Zn, Cr	2–12%	