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Baltica

BALTICA Volume 28 Number 1 June 2015: 1–10
doi: 10.5200/baltica.2015.28.01

Heavy metal pollution of Kotlin Island in the Gulf of Finland

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Kurilenko, V., Osmolovskaya, N., 2015. Heavy metal pollution of Kotlin Island in the Gulf of Finland. *Baltica, 28 (1), 1-10.* Vilnius. ISSN 0067-3064.

Manuscript submitted 6 February 2015 / Accepted 25 May 2015 / Published online 25 June 2015

Abstract The current environmental state of Kotlin Island and coastal areas reflects the negative impact of industry, transport and urban utilities that has lead to increased heavy metal content in soils, in terrestrial and aquatic vegetation and in the water of the Gulf of Finland. Based on the analysis of pollutant metals in roots and shoots of native plants grown on Kotlin Island, species with high metal-accumulating capacity have been identified. Of these, there were dandelion and coltsfoot demonstrating high mobility in heavy metals, especially Zn, upward transfer. These could therefore be promising as bioindicators and phytoremediators of polluted areas pointing to origins of contamination. The presence of heavy metal contamination in the coastal waters of the gulf and its variability along the coastline is regarded as dependent on multiple sources of pollution associated with Kotlin Island, namely industrial and municipal waste waters, ship and vehicle traffic, aerosol deposits, contamination by dredging activity in a new port as well as the result of metals leaching from the soils of the island (Zn, Cu, Ni). Metal-accumulating coastal plants such as cane can be a source of secondary pollution of the gulf waters during their seasonal decomposition. The data showed significantly elevated concentrations of Ni, Zn and Cd in the hair of children living in the town of Kronstadt located on Kotlin Island that confirms the adequacy of the proposed indicating methodology and shows the unfavourable environmental situation in the region.

Keywords *• ecogeology • heavy metals • environment pollution • soil • plants • biogeochemical cycling of metals • bioindication • phytoremediation*

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INTRODUCTION

The Gulf of Finland which is a bay in the eastern part of the Baltic Sea is currently under severe stress owing to a large human population and the environmental effects of both anthropogenic activities as well as the area's special geographical, geological and climatological characteristics. A number of threats to the gulf could be caused by any human activity at sea, on the littoral and in the catchment area. The environmental state of the Gulf of Finland and the major problems that threaten its ecosystems have attracted the attention of many researchers. The monitoring of marine and coastal contamination, conducted within the framework of HELCOM, shows that numerous hazardous substances affect the ecosystems of the Baltic Sea gulfs (HELCOM 2007, 2015). The pollutants, including nutrients, surfactants, oil and heavy metals (Vallius, Leivuori 2003; Żbikowski *et al.* 2007; Vallius 2011; Seisuma *et al.* 2011) are primarily associated with the inflow of industrial and municipal wastewaters and agricultural activities. This leads to the weakening of aquatic ecosystems and their natural capacities of to self-purification.

Heavy metal pollution is one of the most disturbing hazards that cause adverse effects on the ecosystems of the gulf. Particularly alarming are high concentrations of heavy metals in bottom sediments (Vallius, Leivuori 2003; Vallius 2012). However in the Gulf of Finland risks can also come from the acid soils of the coast, contributing to the migration of metals (Zn, Al) with the runoff from catchment areas (Faltmarsch *et al.* 2008).

The basic approach in assessing the environmental state is collection and analysis of information on concentrations of pollutants in ecosystems, in water and bottom sediments in particular (HELCOM 2007). However, this approach seems inadequate for evaluating the joint effect of several toxicants and predicting the degree of their negative impact on living organisms. In this regard, a more promising methodological approach could be the use of chemical methods, along with biological ones, based on bioindication. The suitability of various groups of organisms in the assessment of heavy metal pollution in the coastal zones has been shown in studies using green algae (Zbikowski *et al.* 2007), brown algae (Seisuma *et al.* 2011), macrophytes (Aulio 1986) and plankton as early warning indicators of the environmental status of food chains in the Baltic Sea (Indicators 2013). However, only the joint use of chemical-analytical and biological methods will provide the most complete and unambiguous information on the state of the environment.

Kotlin Island with the town of Kronstadt is located on the western boundary of the Neva Bay of the Gulf of Finland, 30 km West of Saint-Petersburg and is thus included in the ecosystem of the gulf. For three centuries of its history, Kronstadt was the base of the Russian Navy, but in the last 30 years it has lost its military significance. Urban and industrial uses of Kotlin Island have a damaging effect on the ecosystem of the gulf. Heavy metals, which are involved in the biogeochemical processes of migration and have a negative impact on abiotic and biotic components of ecosystems and on human health, are of priority among the polluting substances emitted here into the environment (Belkina 2003; Kurilenko *et al.* 2004). Given the relatively small area and its isolation from Saint-Petersburg, Kotlin Island can serve as a convenient model for environmental problems study of the gulf and for the joint application of chemical and biological methods for assessing the state of the environment.

The purpose of this study was to survey heavy metal content in abiotic (soil, water) and biotic (plant, human) components of the natural environment of Kotlin Island taking into account the indicated role of heavy metals as priority pollutants in the environment.

STUDY AREA

Geological setting

Kotlin Island is located at the junction of two major tectonic structures – the Baltic Shield and the north-western part of the Russian Plate. The surface of the Archean–Paleoproterozoic basement gently dips to the South-East and is overlapped with sedimentary formations of the plate cover. The crystalline rocks are represented mainly by biotite gneisses and granite gneisses, amphibolites and quartzites. Within this tectonic zone a relative displacement of basement blocks is observed whose intensity depends on the period of geologic history.

Subaqueous relief of groundwater in the described area of the Gulf of Finland is effectuated mainly by the pressure of the Gdov aquifer. Discharge of groundwater (with a salinity of about 2–4 g/l) is located in the Gulf of Finland. Everywhere within the coastal zone there are weakly watered technogenic grounds of different grain-size composition (Geological Atlas 2009). They represent a specific environmental hazard. A major part of the island coastal zone is artificially strengthened.

The largest marine-induced hazard in terms of degradation of the coastal zone of the Gulf of Finland is the potential coastline retreat. Intense coastal erosion processes are usually caused by a combination of various natural (mostly geological and hydrometeorological) and anthropogenic factors (Ryabchuk *et al.* 2011).

Natural environment in the Kotlin Island

Assessment of the environmental situation on Kotlin Island has been recently undertaken by several researchers (Belkina 2003; Lyakhin *et al.* 1997; Kurilenko, Osmolovskaya 2007).

In the atmospheric air of the island a particular place among priority pollutants is occupied by heavy metals that are known in the form of organic and inorganic compounds, in the form of dust and aerosols, and in gaseous elemental form (Hg). Aerosols Pb, Cd, Cu and Zn consist mainly of submicron particles with a diameter of 0.5 to 1 μm, while aerosols Ni and Co from coarse particles (>1 μm) are mainly generated from burning coal and diesel fuel (Ivanov 1994).

The surface waters of Kotlin Island and the town of Kronstadt are characterized by pollution mainly with heavy metals and organic substances, such as phenols, oil products, surface-active substances and polychlorinated biphenyls (PCBs). In some cases they enhance the migration of heavy metals due to formation of soluble complex compounds, which contribute to the increase in the waters' content of soluble organic forms of Cd and Ni, forming stable chelate compounds with surfactants (Kurilenko *et al.* 2004). For Hg, Cu, Zn and Pb augmentation of the technogenic sediments fraction was noted, where they are located mainly in the geochemically mobile sorption-carbonate, organic and hydroxide forms. The heavy metals' content in water bodies of Kronstadt is significantly higher than the maximum permissible limits (MPL) for waters of fishery and domestic use in Russia (Lyakhin *et al.* 1997; Control of chemical… 1998), which creates an environmental hazard to human activity and aquatic organisms.

The environmental state of Kotlin Island and Kronstadt has become particularly acute after the building of the dam which protects Saint-Petersburg from floods. Due to the marked reduction (by 25% on average) of water exchange between the Neva Bay and the eastern part of the Gulf of Finland, with a change in the direction of currents and the lack of water passes, the water area around Kotlin Island became much more polluted than in the whole bay. According to G. Y. Belkina (2003) a significant increasing of several pollutants concentrations was marked in the bottom sediments from the harbours of Kronstadt, especially of Hg, phenols and oil products.

Pollution of natural ecosystems with heavy metals, as is known, occurs due to their connections with adjacent watersheds in the form of true solutions, suspensions and colloids in various chemical forms: water soluble; sorption-carbonate; organic; associated with freshly precipitated hydroxides and oxides, and crystalline oxides and hydroxides (Kurilenko *et al.* 2004). Dissolved substances in natural water ecosystems are presented in the form of dissociated and non-dissociated ions, *inter alia* organic molecules, as well as a variety of complex compounds, including chelates of metals with humic acids.

Soils act as one of the most important biogeochemical barriers for most toxicants along the path of their migration in surface and ground waters, accumulating various toxic compounds. The degree of metals' mobility in soil depends on the geochemical environment and the anthropogenic impact level. The migratory ability of metals' cations increases in oxidative conditions, and of anions – in reducing ones. A large part of heavy metals that enter the soil are fixed mainly in the form of organometallic complexes in the upper humus horizons (Kabata-Pendias, Pendias 1992). The high toxicity of heavy metals among the chemical elements is based on the ability of living organisms to bioaccumulate pollutants and on the high affinity of heavy metals to physiologically important organic compounds, which leads to inactivation of the enzymes of metabolism (Prasad 2004; Titov *et al.* 2014).

MATERIAL AND METHODS

Kotlin Island with the town of Kronstadt is an urbanized area, where, along with the natural soils, there are also artificial grounds and earth formed in the process of mixing of natural material (clay, sand, peat etc.) and anthropogenic substances (recycled construction substances, household and industrial waste). In this study soil samples were selected in the central part of Kotlin Island directly in the town of Kronstadt in its recreational, residential and industrial areas and along the coastline of the island.

Sampling of soils and terrestrial plants was performed on-site on Kotlin Island in the summer and autumn of 2011 and 2012. The sites for sampling were selected based on available literature on Kotlin Island pollution and on previous studies (Belkina 2003; Kurilenko *et al.* 2004). The location of the sampling sites is shown in Fig. 1. The sampling sites marked as 8* and 10* correspond to the locations of artificial grounds on the areas of the coastal zone.

Soil samples and samples of plants (dandelion *Taraxacum officinale*, clover *Trifolium pretense* and coltsfoot *Tussilágo fárfara,* roots and shoots separately) were collected by the standard method of envelope with subsequent drying. For each sampling site three parallel samples were collected. Soil samples were air-dried, ground and passed through a sieve with the cell diameter of 3 mm. Analysis of total metal content in soils was performed using the method of X-ray

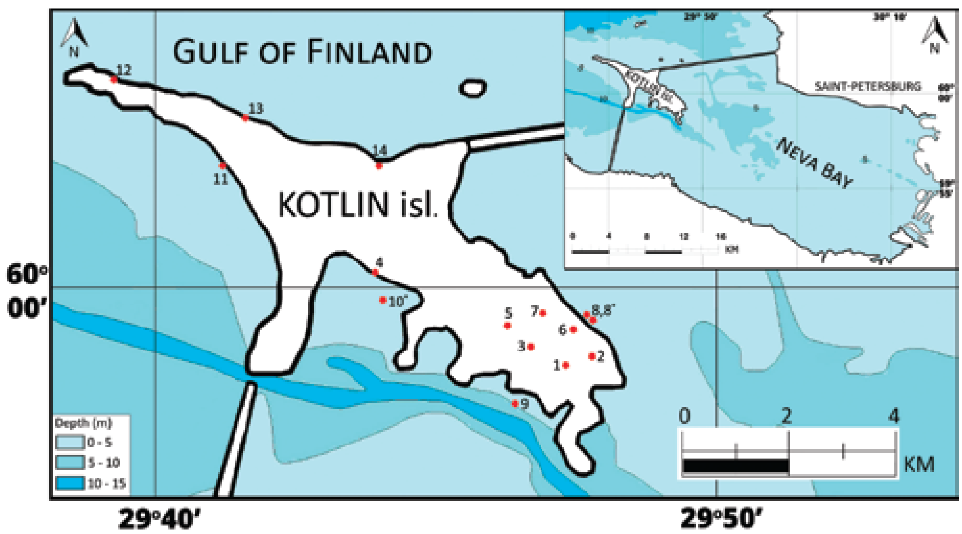

Fig. 1 Study area with sampling sites (bottom topography from Spiridonov, Pitulko, 2000)

analysis on multichannel X-ray spectrum crystal-diffraction analyzer AR-113. The results of the metals analysis were expressed in mg·kg^{-1} of soil.

Samples of plant roots and shoots were gently washed with tap water and then rinsed with deionized water and air-dried for 24 hours at 70°C. Dried plant tissues were ground into fine powder and digested with a mixture of concentrated HNO_3:$HClO_4$ in the ratio 4:1, according to the previously developed technique (Osmolovskaya *et al.* 2007).

The total metal concentrations (Fe, Mn, Zn, Cu, Cr, Pb, Co, Ni, Sr, Ti) in plant material were then determined by using inductively coupled atomic emission spectrometry ICPE-9000, Shimadzu, Japan. The results were expressed in mg·kg^{-1} of dry weight (DW).

Samples of surface water were taken in the coastal zone along the shoreline at a distance of 30–50 m away from the sampling sites 8–14. Samples of reed *Phragmites australis* were collected from water at the site 12 near the Kotlin Island. Analysis of metals in water was performed using the ICPE-9000, Shimadzu, Japan. Analysis of metals in aquatic plants was done using the same methods as in the case of terrestrial plants.

Samples of children's hair selected in the kinder garden in Kronstadt district were cut by parents, packaged and registered, marking the sex of the child, age, place of residence, the presence or absence of chronic diseases of the child and parents, as well as long-term travels anywhere outside of Kronstadt. Heavy metals in hair samples were determined by using X-ray fluorescence spectrometry MXF-2400, Shimadzu, Japan.

Statistical evaluation was applied to the data were presented as the mean ± SD (standard deviation). Biological Concentration Factor (BCF) was calculated as the ratio of metal concentration in plant roots (mg·kg^{-1}DW) to that in the soil (mg·kg^{-1}) as described by Yoon *et al.* (2006). Biological Transfer Coefficient (BTC) was calculated as the ratio of metal concentration in plant shoot (mg·kg^{-1}DW) to that in plant root (mg·kg^{-1}DW) in accordance with Li *et al.* (2007) and Khan and Uzair (2013).

RESULTS

Heavy metals in soils

Soil samples were analyzed for the content of several heavy metals, primarily Fe, Mn, Zn, Cu, Pb. The results indicate that the content of these metals in soils varies greatly among the sampling sites and zones in the town. Data on Fe and Mn content (Table 1) showed that Fe prevailed among the studied metals. In recreational (sites 1–3), residential (sites 5–7) and industrial (site 4) zones concentrations of Fe in soils were mainly in the range 18785–29264 mg·kg^{-1} with exception of much higher value in site 5, whereas in the coastal zone they were lower and amounted to 12375–22175 mg·kg^{-1} except for site 8*. The next one is the content of Mn, its concentrations were also higher in residential and recreational areas in comparison with the coastal zone. At the same time, the concentrations of both metals did not exceed their Clarke values in the Earth's crust (Ilyin 2012), as well as maximum permissible limits (MPL) of their concentrations in soils accepted in Russia (Control of chemical…1998) (Table 1).

Assessment such heavy metals concentrations in soils as Zn, Cu, Pb, Cr, Co, Ni is of special interest, these metals are among the most common pollutants in industrial and urban agglomerations. The data obtained revealed that concentrations of these metals in the examined soils on-site are highly variable. For Zn they were identified in the range of 35–367 mg·kg^{-1}, Cu 30–173, Pb 19–381 (Fig. 2), for Cr 18–75, Ni 10–56 mg·kg^{-1} soil (data not shown) and in some cases significantly exceeded their MPL values accepted for soils (100 mg·kg^{-1} for Zn, 55 for Cu and 32 for Pb) (Control of chemical …1998). The maximum excess over MPL reached 3.1 times for Cu, 3.67 times for Zn and 11.9 times for Pb. Data on Zn, Cu and Pb concentrations in the soils of urban and coastal areas show that the most contaminated with these metals soils are those of the central part of Kotlin Island, predominantly in industrial (4) and residential (5, 6) and partly in recreational (1) areas of the town of Kronstadt with

Table 1 Content of Fe and Mn in soils of Kotlin Island and their reference indices (mg·kg^{-1})

Recreational (1–3), industrial (4) and residential (5–7) areas					Coastal zone				
Sampling sites	Longitude	Latitude	Fe	Mn	Sampling sites	Longitude	Latitude	Fe	Mn
1	29.788	59.989	29170	621	8	29.795	59.996	17783	170
2	29.796	59.990	25239	965	8*	29.797	59.995	41128	543
3	29.778	59.990	18785	696	9	29.773	59.983	13142	185
4	29.732	60.002	24025	805	10*	29.734	59.998	19362	212
5	29.771	59.994	42875	636	11	29.686	60.017	18352	360
6	29.791	59.994	20834	272	12	29.654	60.030	22175	370
7	29.782	59.996	29264	613	13	29.694	60.024	12375	233
					14	29.733	60.018	16655	561
Clarke			42000	1000					
MPL			38000	1500					

less contaminated soils in sites 2 and 3. Along the coastline, minor contamination was observed in the south-western (9) part of the island and in its north–eastern part, closer to the dam (13, 14), where imported soils relatively devoid of contaminating metals dominated. In other sites of the coastal zone moderate contamination with investigated metals was detected in the eastern part (8, 8*), higher contamination was found in the south–western and western parts (10*, 11), in the seaport area, and the highest one was set in the north–eastern tip of Kotlin Island (12).

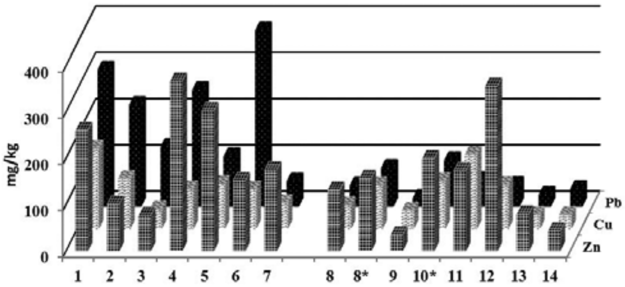

Fig. 2 Heavy metal concentrations in soils of urban (1–7) and coastal (8–14) areas of Kotlin Island (mg·kg^{-1})

The data show that the dominant contaminant metal in the centre of Kotlin Island is Pb followed by Zn and Cu, while the soils of coastal area are polluted primary by Zn and Cu. This strongly suggests contamination is due to specific human activity in this part of the island.

Heavy metals in terrestrial vegetation

Sampling of plants was carried out at the same sites as the sampling of soils in order to study the role of vegetation in the bioaccumulation of heavy metals and their transport through the "soil-plant" chain at the studied area. Also it seemed important to assess the degree of involvement by plants in the maintenance of the metals' biogeochemical cycles in the survey of contaminated areas with respect to the bioindicator role of terrestrial plants and the prospects of their use for phytoremediation of contaminated areas (Pilon-Smits 2005). The most representative among the native species of terrestrial plants were dandelion *Taraxacum officinale*, red clover *Trifolium praténse* and coltsfoot *Tussilágo fárfara*, the choice of which was determined by taxonomic affiliation and abundance within the survey area. Estimation of biogeochemical parameters was carried out based on the analysis of metals' concentrations in roots and in aboveground parts of plants (mg·kg^{-1} dry weight) and on the calculation of the Biological Concentration Factor (BCF) of metal in the roots (Yoon *et al.* 2006) and of Biological Transfer Coefficient (BTC) of metal movement from roots to shoots (Li *et al.* 2007; Khan, Uzair 2013).

According to the soil survey of the Kotlin Island one of the most metal polluted places on the island was site 4 (Fig. 2). All three species of plants were collected at this site and analyzed for the concentration of heavy metals in their organs. In this case in addition to the analysis of Fe, Mn, Zn, Cu, Pb in soil and plants was determined the content of Sr and Cr (Fig. 3), as well as Co, Ni, Ti (Fig. 4, 5). The results presented in Table 2 and Fig. 3 show that the absorption of most of the studied metals was quite intensive in plants and most of the metals accumulated in the roots rather than in the shoots. The most heavy extracted metal was Fe, its concentration in the roots of the red clover reached 29032 mg·kg^{-1}DW whereas in the roots of the dandelion Fe content did not exceed 5302 mg·kg^{-1}DW. The absolute concentrations of contaminating metals in roots differed significantly, but in all species generally decreased in the same following order: Fe>>Mn>Zn>Sr≥Cu>Cr>Pb (Table 2, Fig. 3).

Table 2 The content of Fe in roots and shoots of selected plants, mg·kg^{-1} DW

Plant parts	dandelion	coltsfoot	red clover
Roots	5302 ± 220	10893 ± 530	29032 ± 720
Shoots	898 ± 72	176 ± 12	1340 ± 65

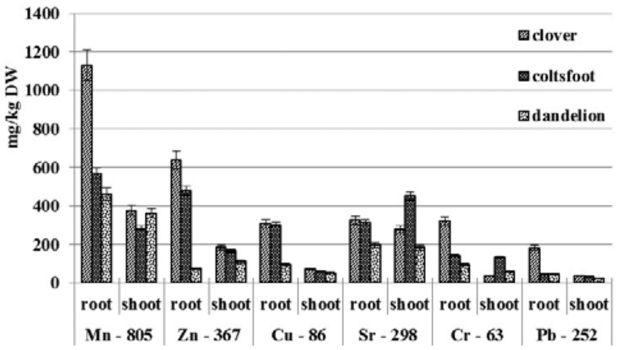

Fig. 3 Heavy metal concentrations in roots and shoots of native plants grown in industrial zone of Kotlin Island (site 4, Fig. 2). The numbers listed below correspond to the concentrations of metals in the soil (mg·kg^{-1}) at the site of survey

Evaluation of the BCF of heavy metals concentration in plant roots in relation to its content in the soil testified that for practically all metals this index reached its maximum in clover, varying from 0.7 for Pb to 3.5 for Cu and Cr (Fig. 4). In roots of coltsfoot the corresponding ratio varied from 0.2 for Pb to 2.2 for Cr and 3.5 for Cu. In dandelion the BCF for Pb was as low as in coltsfoot and the ratios for Cu and Cr were higher (1,1 and 1,5) but less than in other plants. The intensity of Fe, Mn, Zn bioaccumulation in the roots of clover was in the range of 1.2 to 1.75, despite the large difference in the concentrations of these metals in the soil. In coltsfoot roots the corresponding coefficients were in the range of 0.5 (Fe) -1,35 (Zn), in dandelion BCF values for these metals were minimal among the studied species and amounted to 0.2–0.6. Relatively high BCF values for Co (2.6 and 1.35) and Ni (1.7 and 1.5) were found in the roots of clover and coltsfoot, while in dandelion they did not exceed 0.2 and 0.6 (Fig. 4). Sr was accumulated in roots with BCF in the range of 0.7–1.1 and Ti accumulated definitely weaker with BCF values similar to the bioaccumulation of Pb (Fig. 4).

The calculation of BTC as coefficient of heavy metal transport from the roots to the aboveground parts of the plants showed a different pattern in the intensity of these processes in the investigated plant species. The most efficient transfer of metals to the shoots was observed in dandelion, where BTC values for different metals ranged from 0.2 (Fe) to 1.5 (Zn), while in red clover the values of BTC for most metals did not exceed 0.12–0.35, and in coltsfoot they were in the range from 0.05 to 0.9 (Fig. 5).

The highest BTC values among the studied metals were observed for Sr – from 0.85 to 1.45, depending on the plant species, and also for Zn in dandelion (1.45)

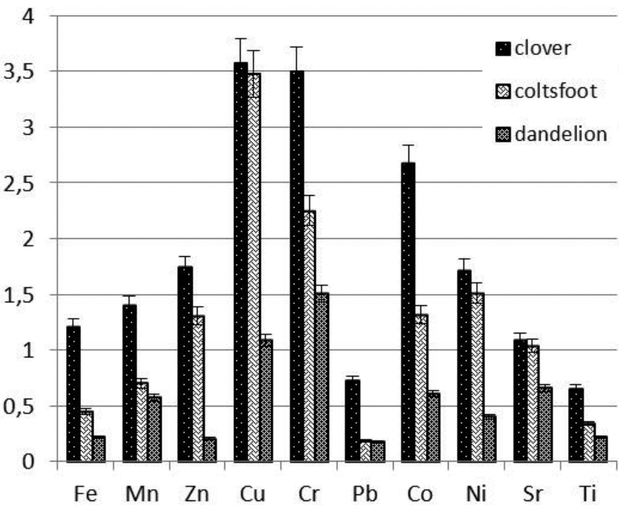

Fig. 4 BCF of heavy metals in plant roots in the "soil-root" system

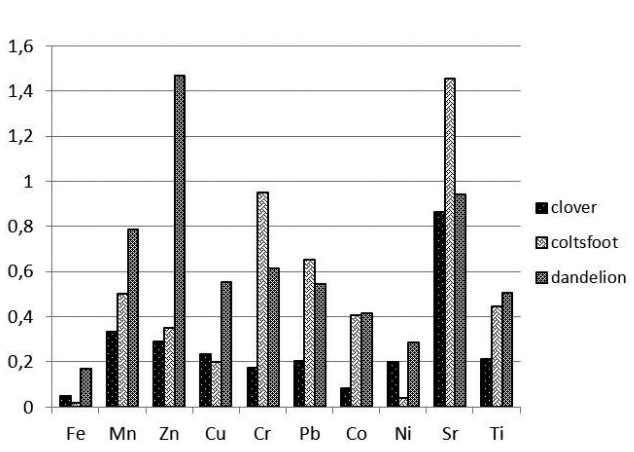

Fig. 5 BTC of heavy metals in plants in the "root-shoot" system

and for Cr in coltsfoot (0.95). While concentrations of most metals in selected plant species at the study area were generally higher in the roots than in shoots, the root barrier role leading to the retention of metals from their transfer to the shoots appeared to be much stronger in respect to Zn and Cu in coltsfoot and in red clover plants than that in dandelion, whereas in the case of Cr and Pb it was mostly observed in red clover (Fig. 3 and Fig. 5). In coltsfoot plants the concentrations of Cr and Pb in roots and shoots, in contrast, differed very little, and the corresponding transfer coefficients of these metals to the shoots were 0.95 and 0.67. In leaves of coltsfoot the concentration of Cr was the highest among the surveyed plants (135 $mg \cdot kg^{-1}$DW).

In general, the obtained data show that dandelion most adequately reflects the degree of anthropogenic load of heavy metals in soils, which is consistent with the observations made by other authors and confirms the prospects of using this plant in phytoindication of environmental pollution by metals (Kabata-Pendias, Dudka 1991; Mikalajūnė, Jasulaitytė 2011; Ligocki *et al.* 2011; Kleckerová, Dočekalová 2014). However, the results showing that the values of BTC for most metals in plants are less than 1.0 suggest that, with respect to wild plants grown in contaminated soils, the mechanisms limiting the toxic metals' movement to the aboveground organs are present and regulate the overall biogeochemical processes of metal transfer in the "soil-root-shoot" system.

Heavy metals in coastal waters and plants

Given the information on the increase of some pollutants' concentrations in the waters and sediments of the Gulf of Finland (Belkina 2003; Vallius 2012), it was of interest to assess the possible impact of Kotlin Island with the town of Kronstadt on the waters and vegetation in the coastal zone of the Gulf of Finland. Data presented in the Table 3 as the concentration ranges of metals in water samples along the perimeter of Kotlin Island showed that for such metals as Fe, Mn and Zn they varied considerably. The differences between minimum and maximum concentrations for individual metals ranged from 1.5 (Cu) up to 100 (Zn) times. To assess the degree of toxicity of established concentrations of metals in the water to biota and humans the data was compared to the specified maximum permissible levels (MPL), approved in Russia for the content of metals in the waters of the fishery and domestic purposes (Control of chemical…1998; Kurilenko *et al.* 2004). Fe concentrations of 3.8–10.3 times over the MPL for fishery waters and 1.3–3.4 times over the MPL for domestic waters were observed at various sampling sites. At the same time, excesses of 4, 10 and 15 times over the MPL for fishery waters were observed in Mn, Zn and Cu content respectively (Table 3). Compared with the MPL for domestic waters no excess in Mn, Zn, Cu or Ni content in the waters of the Gulf of Finland near Kotlin Island was found.

Samples of reed *Phragmites australis* were collected from water at the site 12 near the Kotlin Island coast to analyze the heavy metal content. The analytical data showed high accumulation of Fe in the roots of these plants (7900 mg·kg^{-1} DW), whereas the content of other metals was significantly lower (250 mg·kg^{-1}DW for Mn and 23–12 mg·kg^{-1} DW for Zn, Cu and Ni) (Table 3). In general, the differences in the accumulation of these metals corresponded to the differences in their levels in water.

Analysis of metals in the above-ground parts of reed showed a high content of Fe in the shoots, especially in leaves (up to 750 mg·kg^{-1}DW) and flowers (Fig. 6), which can be explained by its intensive migration from the roots or that is less possible by the absorption through the submerged leaves. The content of other metals in the shoots were mostly within 10–30 mg·kg^{-1}DW, except for about 50 mg·kg^{-1}DW of Mn in the leaves.

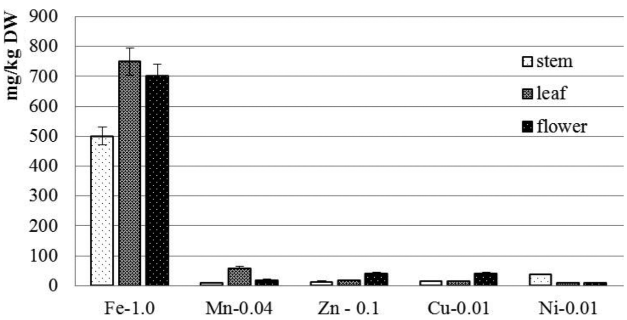

Fig. 6 Heavy metal contents in the aboveground parts of *Phragmites australis* plants in the coastal zone of Kotlin Island in the Gulf of Finland. The numbers below correspond to the concentrations of metals in water (mg·l^{-1}) at the site of survey

Heavy metals in human hair

The health status of people in response to anthropogenic pressure is an important element in the basic assessment of an area's environment state. Therefore, we decided to choose the indicator index used in a medical check-up of people living in contaminated areas. One of the indicators used for point of view can be the assessment of the pollutant content in human organs and tissues. An available human tissue for these purposes is human hair (Furaeva, Eremeyshvili 2006), which may reflect environment pollution by metals. In this regard, we have investigated the content of heavy metals in the hair of children of different ages living permanently in the town of Kronstadt on Kotlin Island and having different forms of diseases. The obtained data were compared with reference values of healthy children.

The data show that concentration of Zn in the hair of girls 7 years old and more exceeds the reference value by 1.7 times (Table 4). The concentration of Ni exceeds the reference value by more than 4 times in the hair of boys more than 7 years old, and is also exceeded in the hair of children of other age groups. Also, a strong (up to 4–10 times) excess over the reference level of Cd was noted in the hair of girls more than 7 years old. At the same time, with a sufficient degree of reliability, we can argue that the concentrations of Cr, Pb and Cu in the hair of children are not significantly higher than their reference levels, while the content of As is significantly above it. As reported by Korjaev and Friedman (2006) for children of younger age in Kronstadt the most commonly encountered are skin and infectious diseases, psychological and behavioural disorders. Among adolescents diseases of eyes, skin and subcutaneous tissue dominate. For adults the most

Table 3 The concentration ranges of heavy metals in the coastal zone of the Gulf of Finland, MPL for metals in fishery and domestic water and maximum concentrations of metals in the roots of reeds on the study site

Metal	Ranges of metal concentrations in coastal zone waters, mg·l^{-1}	MPL for fishery/domestic waters, mg·l^{-1}	Maximum metal content in the roots of reed *Phragmites australis*, mg·kg^{-1} DW
Fe	0.38–1.03	0.10/0.3	7900
Mn	0.008–0.040	0.01/0.1	250
Zn	0.001–0.1	0.01/1.0	23
Cu	0.01–0.015	0.001/1.0	17
Ni	0.01–0.017	0.01/0.1	12

Table 4 Heavy metals in the hair of children living in Kronstadt and their reference values, mkg·g^{-1}

Metal	♂ 6 years	♂ 7 years	♀ 7 years	♀ 8 years	reference values
Zn	88.0	99.0	240.0	140.0	135.8[1]; 50–150[2]
Cu	17.9	18.7	19.0	19.5	11.1[1]; 8–15[2]
Pb	4.9	4.8	2.3	3.0	8.0[1]; 5.0[2]
Cd	2.5	2.5	1.9	4.4	1.0[1]; 0.05–0.40[2]
Ni	2.0	5.6	1.9	2.1	1.17[1]
As	5.0	4.9	4.8	4.9	0.1–1.0[2]
Cr	2.5	2.5	0.3	0.3	0.2–2.0[2]

[1] (Gudkov *et al.* 2004), [2] (Furaeva, Eremeyshvili 2006)

frequent diseases are those of the nervous system and sense organs. It is possible that some of these diseases may be at least partly caused by the adverse environmental state including metal pollution.

DISCUSSION

According to HELCOM (2010) pollution by hazardous substances is identified as one of four main issues requiring actions to improve the health of the Baltic Sea and heavy metal pollution is among them. Kotlin Island is included in the ecosystem of the Gulf of Finland that is why the study of its pollution with heavy metals is essential for the assessment of the environmental situation in the gulf. The results of the study showed that soils of Kotlin Island, especially urban soils in the central section, are contaminated by heavy metals. In agreement with the work of other authors (Vinberg, Gutelmaher 1987; Belkina, 2003), critical metals are Zn, Cu and Pb whose concentrations show considerable variation. Pollution can be a result of the industrial and municipal waste intake to the environment from the town of Kronstadt located on the island as well as a consequence of the prolonged presence of the naval base of the Russian fleet at Kotlin, which now has lost its strategic significance. However, data showing that the main pollutant is Pb (its excess over MPL is up to 11.5-fold compared with 3.1 for Cu and 3.67 for Zn) suggests that the principal contribution to the current pollution of Kotlin Island can be explained by heavy traffic. The risk of soil contamination with metals to humans and biota is realized through the metal ability to migrate in soils, surface waters and air. The harmful effect of metal polluted soils of the island to humans is primarily due to air transfer of contaminated soil particles, their penetration in the human body during breathing and deposition on human skin and hair. The data on elevated concentrations of some heavy metals in the hair of children living in the town of Kronstadt on Kotlin Island confirm the adequacy of the proposed indicating methodology (Gudkov *et al.* 2004; Furaeva, Eremeyshvili 2006) for the environmental state assessment in the populated area.

Metals' mobility in soils and their transfer to plants also has bioindicative value (Kabata-Pendias, Pendias 1992). The data on heavy metal accumulation in roots and in aboveground parts of native terrestrial plants sampled on Kotlin Island provides evidence for the active involvement of urban vegetation in metals' biogeochemical mobility via the «soil-plant» system. The data obtained regarding the accumulation of metals in dandelion and red clover plants are consistent with data of other authors (Kabata-Pendias, Dudka 1991; Mikalajūnė, Jasulaitytė 2011; Ligocki *et al.* 2011). These studies consider the important role of these species as bioindicators of environmental pollution with heavy metals and the prospects of their use for remediative purposes. Based on the results of the distribution of metals in plant organs, it can be assumed that the strategy of protection from toxic metals inherent in these plants is partly realized via metals binding in the cell walls of plant roots (Titov *et al.* 2014). However, another process related to the intracellular detoxification of heavy metals via the formation of organic-chelate complexes in leaves and other parts of plants also exists (Prasad 2004). As one can assume from the data obtained that dandelion is best suited to the latter strategy among the species studied with the highest transfer coefficients of the upward Zn and Mn migration while in the case of Cr and Pb this strategy was better manifested in coltsfoot. This issue, however, requires further research.

It should be noted that accumulation of heavy metals in urban plants is discussed here primarily in connection with the assessment of their possible involvement in biogeochemical processes on the contaminated area. In general, urban plants contaminated with metals do not pose a direct danger to humans, as they are not used as food, but they can pose a risk to herbivorous and domestic animals. Metals can partly evaporate from the leaf surface in the process of transpiration. On the other hand, given the current demand in the technologies of phytoremediation for cleanup of soils contaminated with heavy metals (Pilon-Smits 2005), our data show that the examined urban plants have certain potential for phytoremediation. Dandelion and coltsfoot among them as plants with more pronounced movement of metals to the shoots and Zn especially present a greater potential for cleaning an environment subject to metal pollution.

Recently much attention has been paid to heavy metal pollution with respect to the quality of bottom sediments in the Baltic Sea (Vallius, Leivuori 2003; Vallius 2011, 2012; HELCOM 2007, 2010). Once released into the sea waters, metals can remain there for long periods. Much less information is available regarding the concentrations of metals in the waters of the gulf. Our data on metal contents in the coastal waters of the Gulf of Finland showed high variability depending on the sampling area. In some cases the concentrations were above the MPL for fishery waters (Control of chemical…1998; Kurilenko *et al.* 2004) that may depend on metals partial runoff from the surface of the island. However, comparing the established metal concentrations with their MPL levels for domestic water, it seems that they do not pose an environmental risk to humans.

A marked seasonal variation of heavy metals in the waters of the Baltic Sea was discovered recently by Daniszewski (2013) near the Wolin Island in Poland. The concentrations of such metals as Zn, Cu, Ni in the surveyed part of the sea were considerably higher (up to 3.9; 2.8 and 0.09 mg·l^{-1} for Zn, Ni and Cu) in comparison with up to 0.05; 0.017 and 0.015 in our study. According to the hydrological work performed in 2007–2010 in the Eastern Gulf of Finland (http://enviropark.ru), the concentrations of the examined metals in the coastal waters of the gulf and its bays around Saint-Petersburg are subject to significant fluctuations, the variation within 1–251mg·l^{-1} for Mn, 20–310 for Fe, 8–98 for Zn and 1–19 for Cu were shown. The concentrations of these metals in the coastal waters of Kotlin Island represented in our study are significantly below the above maximum values, except for Fe.

The observed bioaccumulation of metals in the organs of *Phragmites australis* plants confirms the previously discussed biogeochemical role of this macrophyte and its value as indicator in water pollution assessment (Kurilenko, Osmolovskaya 2006, 2007). The recorded levels of Fe and Cu in *Phragmites australis* leaves were somewhat higher than that previously shown for the estuary in western Finland (Aulio 1986), the content of Zn, and especially Mn, were on contrary significantly below. However, given the seasonal distraction of plant residues with subsequent formation of bottom sediments the inclusion of vegetation in the secondary pollution of the waters of the gulf should be considered.

CONCLUSIONS

The results of the research show that the current environmental state on Kotlin Island and in the coastal areas of the Gulf of Finland reflects the negative impact of industry, traffic and utility systems of the town of Kronstadt that has lead to the accumulation of heavy metals in soil and water environment. Based on the study data, species of native plants with high accumulating capacity for a number of polluting heavy metals are identified, which indicates the participation of these species in biogeochemical migration of metals in the "soil-plant" system. The data suggest considering the studied species for phytoremediation of polluted urban areas, taking into account the specifics of contamination. The analysis of metals in the hair of children identified an excess above the reference levels for Ni, Zn and Cd, that confirms the bioindicator value of this methodology for the purposes of environmental surveys in the contaminated areas. Elevated concentrations of some heavy metals in the coastal waters near Kotlin Island could be due to multiple sources of pollution including industrial and municipal waste waters, ship and vehicle traffic, aerosol deposition, contamination by dredging activity in new port as well as the result of metals leaching from the soils of the island (Zn, Cu, Ni). Reed as aquatic macrophyte can also be a source of secondary pollution of the waters in the Gulf of Finland during seasonal destruction.

ACKNOWLEDGEMENTS

This work was supported by Science Foundation of Saint-Petersburg State University: «Ecological basis of the quality of life in the metropolis» (Grant No. 0.37.79.2011). The authors would like to thank Dr. Walker Trimble (St. Petersburg) for language revision and peer-review referees for their criticisms and valuable suggestions.

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