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Geoecological Assessment of Small Rivers in the Big Industrial City Based on the Data on Heavy Metal Content in Bottom Sediments

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Abstract—The analysis of heavy metal concentration in the bottom sediments of water bodies located within large urban areas is an important component of the monitoring of urban ecosystems. Presented are the results of studying the concentration of heavy metals (by mass spectrometry) in the channel and floodplain river sediments in Petrozavodsk (the Republic of Karelia). It is found that the floodplain sediments of the Lososinka River and the fluvial sediments of the Neglinka River are characterized by the highest level of contamination in terms of the total pollution index Z_c. High values of the geoaccumulation index I_{geo} (>2–3) for lead, zinc, cobalt, nickel, and copper classify the bottom sediments of the urban river stretches of Petrozavodsk as moderately and heavily polluted.

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INTRODUCTION

Petrozavodsk (the capital of the Republic of Karelia) is a big administrative, industrial, scientific, and cultural center in the northwest of Russia. The population of the city is about 270000 (as of 2013). The city is located on the shore of Lake Onega and stretches along the Gulf of Petrozavodsk from southeast to northwest for 25 km (Fig. 1) [5]. The basis of the city industry in the electric power industry (62% of the total volume of production), machine building and metal working (18%), the food industry (13%), and woodworking industry (3%). Besides, Petrozavodsk is the major traffic center through which trains to St. Petersburg, Murmansk, Sortavala, and Kostomuksha pass; the federal highway St. Petersburg–Murmansk is located nearby the city.

Water bodies located in the urban areas are the most vulnerable targets for different pollutants coming from the catchment area. Such water bodies in Petrozavodsk are two small rivers: the Lososinka River (the length is 25 km, the catchment area is 302 km^2) and the Neglinka River (14 km and 46 km^2). Their lower reaches are located in the central part of the city. The average annual water discharge in the estuaries of the rivers is 3.7 m^3/s for the Lososinka River and 0.51 m^3/s for the Neglinka River. About a half of the annual runoff falls on spring (42 to 57% of annual runoff) [1].

The scientists from the Karelian Research Center of Russian Academy of Sciences and Petrozavodsk State University in different years investigated the impact of the urban environment on the water ecosystems of these rivers. The studies focused on aquatic organisms and the physical and chemical characteristics of water in the Petrozavodsk rivers [1]. Insufficient attention was paid to the investigation of the concentration and distribution of heavy metals as the most dangerous pollutants of water bodies [8] in the Lososinka and Neglinka rivers. Thus, the objective of the present paper is to assess the Petrozavodsk rivers based on the data on heavy metal content in the bottom sediments of urban water courses.

Bottom sediments are the reliable indicators of the long-term pollution of water bodies situated in the areas with anthropogenic disturbances which certainly include the areas of big industrial cities [4, 14, 18]. Bottom sediments of fresh water bodies located in urban areas and nearby metallurgical and chemical works, are almost completely modified by technogenesis [9]. Anthropogenic silts are a special type of fresh-water bottom sediments (most often the term is applied to rivers) which differ from background sedi-

Fig. 1. Schematic map of the research area.

ments by the high content of fine-dispersed grain-size fractions and concentration of such dangerous toxicants as Cu, Ni, Pb, Cd, As, Cr, Hg, etc. [13, 14]. Besides, urban water bodies are entirely eutrophied that provokes the high content of organic matter in bottom sediments that easily sorbs the metals coming to the water body (water course) [15].

The basic factor affecting the enrichment of bottom sediments in water bodies with different mineral and organic substances is the surface runoff from the adjoining territory. So, the sediments under study can indicate not only the geoecological conditions of the ecosystem but also conditions in the whole catchment area.

OBJECTS AND METHODS OF RESEARCH

The samples of bottom sediments of the Lososinka and Neglinka rivers were taken within the city and in the suburban conditionally background zone during the summer field work in 2011 following the generally accepted methodological recommendations (Fig. 1) [3, 7]. The samples were taken along the full length of the Petrozavodsk rivers with the step of 100–200 m. The upper (0–10 cm) layer of bottom sediments was investigated. The sampled sediments are mainly represented by the channel facies, and the floodplain bottom sediments are observed in the artificially regulated parts of the Lososinka River (Meretskov and Fontan stretches). The urban parts of Lososinka and Neglinka and the suburban parts of both rivers where the sediments are represented by the channel facies, were singled out in a separate group. In total, 117 samples of Petrozavodsk river sediments were studied. The samples were dried to the dry-air state. The maximum preservation of the clay fraction was achieved by the following procedure: the liquid part of a sample was dried separately in Petri glass dishes which were preliminarily washed with distilled water. The sieving of samples was carried out using the standard sieve with the cell size of 0.1 mm. The chemical composition of the argillaceous-silt fraction of bottom sediments is a reliable indicator of the pollution of water ecosystems because it is caused by the processes of anthropogenic nature in the areas with anthropogenic disturbance [11, 17].

The determination of the concentration of Fe_{tot} in the samples of bottom sediments was carried out using the ARL ADVANT'X X-ray fluorescent spectrometer. The ignition loss was determined by the weight method after the samples under study had been heated up to the temperature of 1100 C. The content of Pb, Sb, Cu, Zn, Co, Mo, and Ni in the samples from the Lososinka and Neglinka rivers was determined by the mass spectrometry method using the X Series-2 ICP-MS instrument. To check the correctness of the sample analysis, the standard sample of the chemical composition of Lake Baikal bottom silt BIL-1 was used (GSO 7126-94).

The statistical processing was carried out using the Microsoft Excel 2007 software. The EasyCapture 1.2.0 and Inkscape 0.48.4 software was used for the visualization of the results. To assess the level of contamination of bottom sediments with heavy metals, the total pollution index Z_c and the geoaccumulation in-

Table 1. Concentration of heavy metals (mg/kg) in the bottom sediments of the Petrozavodsk rivers

Parameter	Pb	Zn	Co	Ni	Cu	Sb	Mo	W
Neglinka River (urban part), $N = 40$								
Me	**31.0**	**159.3**	**17.8**	**29.8**	**74.0**	**1.2**	**1.1**	**3.7**
x_{max}	*101.4*	296.1	28.1	43.2	*178.2*	3.8	*5.3*	*20.8*
x_{min}	18.1	70.8	11.5	22.0	34.2	0.3	0.6	1.0
S_{Me}	10.0	63.2	4.3	4.8	28.2	0.5	0.3	1.8
Lososinka River (Fontan stretch), $N = 20$								
Me	**37.9**	**160.3**	**16.9**	**27.8**	**54.5**	**1.4**	1.0	**2.5**
x_{max}	79.4	261.2	24.1	40.6	119.5	3.3	1.5	5.9
x_{min}	20.1	66.2	11.2	17.3	21.9	0.4	0.5	0.9
S_{Me}	11.9	65.3	3.5	4.1	24.5	0.5	0.3	1.3
Lososinka River (Meretskov stretch), $N = 18$								
Me	**18.3**	**117.3**	**19.0**	**27.0**	**31.5**	**0.4**	**0.8**	**1.1**
x_{max}	30.3	*354.4*	24.0	36.6	81.1	1.8	1.2	4.9
x_{min}	14.2	60.3	9.7	17.9	19.1	0.2	0.4	0.3
S_{Me}	3.4	51.2	6.2	7.1	16.8	0.3	0.2	0.6
Lososinka River (urban part, channel facies), $N = 17$								
Me	**14.8**	**67.7**	**10.5**	**16.9**	**19.6**	**0.3**	**0.3**	**0.3**
x_{max}	50.5	172.8	15.7	30.8	80.1	1.9	0.8	2.4
x_{min}	10.6	43.2	7.5	13.3	12.4	0.1	0.0	0.1
S_{Me}	2.9	17.4	2.5	3.3	4.8	0.2	0.2	0.3
Suburban conditionally background zone (both rivers), $N = 18$								
Me	13.1	37.3	7.5	16.4	12.5	0.1	0.4	0.3
x_{max}	28.1	63.7	10.6	20.7	28.2	1.6	0.8	0.6
x_{min}	11.1	19.2	3.7	10.1	6.3	0.1	0.2	0.2
S_{Me}	1.1	15.6	3.7	3.4	5.8	0.1	0.1	0.1

Note: Me is the median; x_{max} and x_{min} are the maximum and minimum values of the sample; S_{Me} is the standard deviation of the median; N is the number of variants in the sample.

dex I_{geo} were used [2, 16]. To compute the values of the total pollution index, the content of one or another metal at the separate measurement point was taken into account if the concentration factor (K_k) of the chemical element turned out to be >1. The concentration factor was computed as the ratio of the chemical element concentration in the bottom sediment sample in the urban environment to the median content of the corresponding metal in the sediments of the conditionally background zone.

RESULTS AND DISCUSSION

The minimum median values of heavy metal concentration in all urban stretches of the Petrozavodsk rivers (Table 1) were registered in the channel bottom sediments of the Lososinka River (the areas of Golikovka and a park close to the former Onega Tractor Plant). The concentration of Pb, Ni, Sb, Mo, and W in these urban sediments is close to the conditionally background one referred to the suburban zone of both rivers under study. The median content of these elements in the bottom sediments of suburban stretches of water courses and in the urban channel sediments of the Lososinka River is close to the mean concentration of presented metals in the soil cover of horizons O and E of the territory of Karelia [12].

It is interesting that the bottom sediments of the Neglinka River which are mainly represented by the channel facies are most of all enriched with such metals as Zn, Ni, Cu, Sb, Mo, and W. High median values of the concentration of Pb, Zn, Co, Sb, and Mo were registered in the sediments of the regulated parts of the

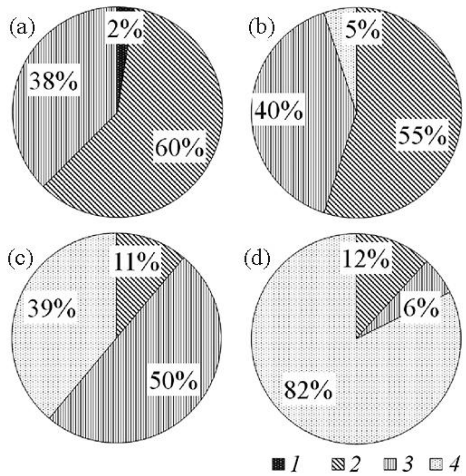

Fig. 2. Percentage of samples with the different level of pollution of bottom sediments in different urban stretches of the Petrozavodsk rivers. River stretches under study: (a) Neglinka River, the city; (b) Lososinka River, Fontan stretch; (c) Lososinka River, Meretskov stretch; (d) Lososinka River, the city (channel). Levels of anthropogenic pollution: (*1*) very high, (*2*) high, (*3*) moderate, and (*4*) low.

Lososinka River (Pb, Zn, Sb, and Mo in the Fontan stretch and Co in the Meretskov stretch). The extreme values of concentrations of some heavy metals should also be noted; they exceed the median content of the elements in the studied samples by several times. For example, the maximum content of Pb for both water courses (101.4 mg/kg) was registered in the sample of the bottom sediments of the Neglinka River taken in the center of the city. The anomalous concentration of Pb (79.4 mg/kg), Cu (119.5 mg/kg), and Zn (261.2 mg/kg) were registered in the sample taken in the regulated stretch Fontan of the Lososinka River in the area where the water course transits from the basic hydrological regime to the reservoir [10]. The abnormal content of Zn (354.4 mg/kg) being maximum for both Petrozavodsk rivers was registered in the sample taken in the floodplain zone of the Lososinka River in the Meretskov stretch. As to the bottom sediments of the Neglinka River, the extreme concentration of Mo (5.3 mg/kg) was registered in the area of the conventional border between suburban and urban stretches of the river; the extreme concentration of W (20.8 mg/kg) and Cu (178.2 mg/kg) were found in the sample taken in the area of the road bridge (the central part of the city).

According to the data of the comparison of heavy metal content using the Mann–Whitney test, the single level of the concentration of Co and Ni was registered for the channel bottom sediments in the urban stretches of the Neglinka and in both regulated stretches of the Lososinka River. The single level of the content of Pb, Zn, Sb, and Mo was registered only for the Neglinka River and for Fontan stretch of the Lososinka River. Both regulated parts of the Lososinka River under study are characterized by the single level of accumulation of Co and Ni. As to other metals, the statistically significant difference between two data samples was revealed ($U_{\text{emp}} < U_{\text{cr}}$). The largest difference in the level of accumulation in bottom sediments in all urban stretches of the Petrozavodsk rivers under study was registered for Cu and W which are most intensively accumulated in the channel sediments of the Neglinka River.

It was revealed that the level of pollution of bottom sediments and, hence, of the whole river increases downstream for both water courses, i.e., closer to the river estuaries and, hence, to the Gulf of Petrozavodsk of Lake Onega (that causes the increase in the level of pollution of this large water body). The maximum values of Z_c were obtained for the part of the Neglinka River flowing in the center of the city where the river crosses the streets characterized by the significant traffic flow. Since in the latter area (under the road bridge) the maximum value of Z_c (129) was registered, this part of the Neglinka River can be defined as an area with the very high level of anthropogenic pollution. The majority of the investigated stretches of the Neglinka River are characterized by the high and moderate levels of the urban river contamination (Fig. 2). Approximately the same results were obtained for the bottom sediments in the regulated part Fontan of the Lososinka River.

According to the computed values of Mann–Whitney test (Table 2), the bottom sediments of the Fontan stretch of the Lososinka River and channel sediments of the urban part of the Neglinka River are characterized by the same level of pollution ($U_{\text{emp}} > U_{\text{cr}}$ at $p < 0.01$).

Table 2. Assessment of differences between the samples of the values of Z_c for different urban stretches of the Petrozavodsk rivers

River, stretch under study	Lososinka River		
	Fontan	Meretskov	City (channel)
Neglinka River, the city	**314** (251*, 294**)	**93.5** (221*, 261**)	**36** (206*, 245**)
Lososinka River, Fontan		**64.5** (100*, 123**)	**24** (93*, 115**)
Lososinka River, Meretskov	**64.5** (100*, 123**)		**65** (82*, 102**)

Note: The table presents the computed values of U_{emp}; the critical values U_{cr} are given in brackets (* at $p < 0.05$; ** at $p < 0.01$).

The values of Z_c of the bottom sediments of another regulated part of the Lososinka River, the Meretskov stretch, vary from 4 to 49 (the median is equal to 13). The majority of the studied samples are characterized by the moderate and low level of pollution. Channel bottom sediments in the urban stretches of the Lososinka River sampled in the area of the city green belts are mainly characterized by the low level of anthropogenic pollution ($Z_c < 10$). The high level of contamination of the water course under study was registered only in the area where the river flows under the road bridge. The median value of the total pollution index of bottom sediments of the Lososinka River in the mentioned areas is equal to 4 (varying from 1 to 34). According to the Mann–Whitney test, the samples of the values of Z_c of all urban stretches of the Lososinka River under study differ statistically significantly at the reliability level of 99% (Table 2). This fact indicates that the floodplain bottom sediments of the river are the "easiest targets" for heavy metals coming to the water course because they contain more fine-dispersed factions of sediments as compared with the channel sediments. Besides, the closeness of highways to the river and the density of the network of storm drains carrying the significant amount of pollutants from the catchment area to the river ecosystem, are of great importance for the accumulation of pollutants.

It should be noted that the level of pollution of channel bottom sediments in the urban part of the Neglinka River in terms of Z_c also differs statistically significantly (i.e., it is higher) from the level of pollution of channel sediments in the urban stretches of the Lososinka River and of the sediments in the regulated Meretskov stretch of the river ($U_{emp} << U_{cr}$ at $p < 0.01$). This circumstance enables concluding the higher pollution of the Neglinka River as compared with the Lososinka River [6] because the organic matter in bottom sediments along with iron compounds is one of the main carriers of heavy metals coming to the water body with the surface runoff. All heavy metals investigated in the bottom sediments of Petrozavodsk rivers have a close and statistically significant positive correlation both with Fe_{tot} and with the ignition loss parameter being a quantitative indicator of the gross content of organic matter in the bottom sediments [4] (Fig. 3). The bottom sediments in the Fontan near-estuary stretch of the Lososinka River is a peculiar barrier for the inflow of pollutants further down the stream, i.e., to the Gulf of Petrozavodsk. However, it is obvious that a part of heavy metals migrate to the lake and are accumulated in the surface layer of its bottom sediments.

The maximum values of the index I_{geo} are typical of the bottom sediments in all urban stretches of Petrozavodsk rivers under study for Pb, Zn, Co, Ni, and Cu (Table 3). The pollution of river sediments with Zn (all parts of water courses under study) and Ni (the Neglinka River only) is assessed as heavy pollution ($I_{geo} > 3$). The rest of the values presented in the table testify the moderately heavy contamination of the Lososinka and Neglinka rivers. The geoaccumulation indices for Sb, Mo, and W correspond to the weak pollution of river sediments with these elements ($I_{geo} < 0$). Thus, the elements of the 1st and 2nd classes of danger, namely, Pb, Zn, Co, Ni, and Cu should be considered as the primary pollutants of the ecosystems of the small rivers Lososinka and Neglinka.

CONCLUSIONS

The content of heavy metals was investigated in the channel and floodplain sediments of the rivers in Petrozavodsk, a big industrial and traffic center in the northwest of Russia. The research revealed that the areas where river sediments are most significantly polluted with different metals, are the floodplain urban stretches of the Lososinka River (Fontan and Meretskov) and the urban stretches of the Neglinka River whose sediments are mainly represented by the channel facies. The single level of accumulation of Co and

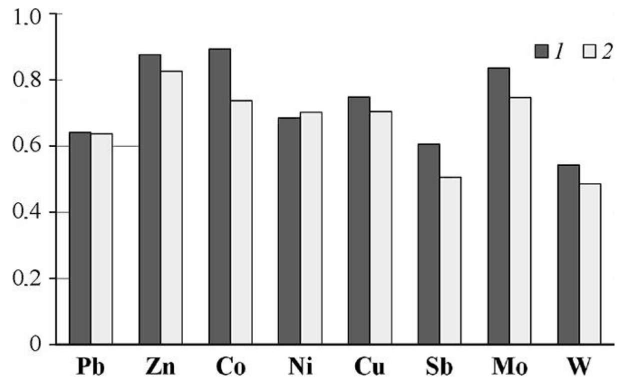

Fig. 3. The values of correlation coefficients of heavy metals in the bottom sediments of the Petrozavodsk rivers with (*1*) iron and (*2*) the ignition loss parameter.

Table 3. Median values of the geoaccumulation index I_{geo} for the bottom sediments of the urban stretches of the Petrozavodsk rivers

Element	Neglinka River, the city	Lososinka River		
		Fontan	Meretskov	City (channel)
Pb	2.74	2.82	2.51	2.41
Zn	**3.90**	**3.90**	**3.77**	**3.53**
Co	2.25	2.23	2.88	2.02
Ni	**3.09**	2.78	2.77	2.57
Cu	2.96	2.96	2.72	2.51
Sb	–0.67	–0.61	–1.10	–1.28
Mo	–0.21	–0.22	–0.33	–0.70
W	0.15	–0.02	–0.40	–0.91

Ni in bottom sediments is typical of the urban part of the Neglinka River and both regulated stretches of the Lososinka River. The same level of the concentration of Pb, Zn, Sb, and Mo was registered only for the Neglinka River and for the Fontan stretch of the Lososinka River.

The maximum values of the total pollution index of bottom sediments Z_c were registered for the channel sediments of the Neglinka River flowing in the central part of Petrozavodsk and in the floodplain sediments of the Lososinka River in the Fontan near-estuary stretch. These stretches should be referred to the most polluted in the whole urban area, especially in its central part being the catchment area for the lower reaches of the investigated water courses (before they flow into Lake Onega). High values of geoaccumulation index I_{geo} for Pb, Zn, Co, Ni, and Cu enable classifying the bottom sediments in the urban stretches of Petrozavodsk rivers as moderately and heavily polluted. The mentioned heavy metals should be considered as the primary pollutants of the ecosystems of both rivers and their catchment basins.

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