

Correlation analysis of heavy metals content in bottom sediments of the shallow zone Sheksninskaya spur of the Rybinsk reservoir in the city of Cherepovets (Russia, Vologda oblast)

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Abstract. The paper presents the results on the content of heavy metals in the bottom sediments of shallow areas of the Sheksninsky spur and the correlation dependences on the content of heavy metals. Significant differences in the content of heavy metals on different banks of the Sheksninsky spur were found only for lead ($p=0.042$). The matrices of paired correlations were constructed, the analysis of which showed that a greater number of dependencies with heavy metals were found on the right bank. The sorption of mercury by organic matter plays a greater role than the sorption of other elements, the correlation is significant $r=0.70$. Single exceedances of maximum permissible concentrations (MPC) of lead and copper in bottom sediments of the right bank were detected. Exceedances of element clarks determined for the earth crust were observed for lead, zinc, copper for bottom sediments of the right bank. A decreasing series of distribution of heavy metal concentrations in bottom sediments of the Sheksninsky spur was determined.

Bottom sediments play an important role in the formation of the chemical composition of natural waters, they also determine many features of the ecology of water systems [1] and are one of the most informative objects of studying the environmental assessment of hydro ecosystems [2]. Of great interest is the study of the influence of bottom sediments on water pollution, since even if the flow of pollutants into watercourses is completely stopped, bottom sediments will remain a secondary source of water pollution for a long time. In most studies, the assessment of the quality of sediments is usually limited to determining the level of pollutants. Of the many toxicants that enter watercourses, heavy metals, which are included in migration cycles, can accumulate in living organisms of aquatic ecosystems, to such concentrations that they begin to have a toxic effect on them, are of particular importance [3].

In bottom sediments, the concentration of heavy metals is higher than in water, which is determined by their rapid transition from the dissolved state to suspensions with high sorption capacity. Changes in the conditions for the accumulation of heavy metals in

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bottom sediments can cause the migration of metals from the sediment layer into the water, which will lead to secondary pollution [4]. An active role in this is played by the upper, most mobile layer with a thickness of 0-10 cm, which is directly involved in the interaction of the two media, since metal concentrations are often increased in the upper layers [5].

It is the shallow areas of water bodies that are the barrier zones through which biogenic and polluting substances come from the catchment area and are included in the biotic cycle. Despite this, shallow water zones are poorly studied and explored.

The purpose of the work: to obtain data on the content of heavy metals (Cu, Fe, Cd, Mn, Pb, Hg, Zn) in the bottom sediments of shallow areas of the Sheksninsky spur and to identify correlations on the content of heavy metals.

The material was collected during the open water period (May-October) in shallow areas from the upper layer of bottom sediments (0-5 cm., sand and sand silt fractions) two meters from the water's edge (at a depth of 1-1.5 m) at 6 stations on the left and right banks of the Sheksninsky spur.

To study the concentration of heavy metals (Pb, Zn, Cu, Cd, Mn, Fe) in the bottom sediments, the method of atomic absorption spectrometry (at MGA-915MD) with preliminary sample preparation at the MINOTAUR-2 mineralizer was used. The mercury content in the bottom sediments was determined on the mercury analyzer "RA-915M" with the prefix "PYRO-915+" by the atomic absorption method of cold steam without preliminary sample preparation. The amount of organic matter in the bottom sediments was determined by the loss of dry soil mass after calcination at 560-600°C [6]. For statistical processing of the obtained data, Microsoft Excel and Statistica programs were used. Since there are no approved environmental standards for the content of trace elements in bottom sediments, when analyzing the results obtained, we used the MPC for soils [7], "Norms and criteria for assessing the contamination of bottom sediments in St. Petersburg Water bodies" [8], which has a regional status, and Clarks of elements [9, 10].

The city of Cherepovets is located in the southwestern part of the Vologda region, on the banks of three rivers belonging to the basin of internal flow: Sheksna, Yagorba and Serovka [11]. Currently, Cherepovets is a major industrial center of the North-West of Russia with a population of more than 315 thousand people. The city is home to large enterprises of heavy and light industry, in addition to them, there are enterprises of metalworking, textile, shipbuilding, woodworking, food and other industries that cause a high level of air pollution and other natural environments. The developed infrastructure of the city is characterized by the presence of almost all types of transport – road, rail, air and river [11]. The entire water area of the northern part of the Sheksninsky Ples and the small rivers of this area are under the powerful influence of Cherepovets. It receives heated city water, a large amount of organic compounds of domestic and industrial origin. Urban runoff spreads over a distance of more than 11 kilometers along the Sheksna River, and the effect of wastewater in the ples is manifested at a distance of up to 25-55 kilometers. The lower course of the Sheksna River has a significant influence on the formation of the waters of the northern part of the Sheksna Ples of the Rybinsk reservoir, and is strongly affected by the tributaries and overlying sections of the Sheksna reservoir [12].

The content of heavy metals in the bottom sediments of the left and right banks of the Sheksna spur varied in the following limits: Pb from 0.01 to 33.72 mg / kg; Zn from 0.36 to 72.83 mg / kg; Cu from 0.01 to 279.28 mg / kg; Cd from 0.001 to 0.21 mg / kg; Mn from 0.04 to 221.53 mg/kg; Fe from 33.65 to 1512.21 mg/kg; Hg from 0.0008 to 0.023 mg / kg. The average actual content of the studied heavy metals in the bottom sediments on the left bank is 2.3 times higher than in the bottom sediments on the right bank. Probably, it is connected with the fact that the intensive longshore movement of water masses on the right bank contributes to leaching of substances from bottom sediments. However, the metal content did not exceed the MPC values of the gross forms for soils, with the exception of

single concentrations of lead (33.7 mg / kg at a MPC of 32 mg / kg) and copper (279.28 mg/kg at a MPC of 55 mg/kg) in the bottom sediments of the right bank. The excess of the Clarks of the elements defined for the earth's crust was observed for lead, zinc, and copper for the bottom sediments of the right bank. According to the norms and criteria for assessing the pollution of bottom sediments in the water bodies of St. Petersburg, the levels of pollution are also determined. Concentrations of all metals were observed below the target level at which the bottom sediments are considered clean. The exception was the copper content (more than 190 mg / kg): a single recorded value exceeding the MPC was higher than the level requiring intervention. Low concentrations of Cd, Hg и Mn indicate their origin mainly from natural sources [13].

The average content of elements in the bottom sediments decreases in the series: Fe > Mn > Zn > Cu > Pb > Cd > Hg. Similar series (Zn > Cu > Pb > Cd > Hg) can be compiled relative to the metal content in the soils around the Cherepovets industrial center [14]. According to the Mann-Whitney criterion, significant differences in the content of the studied elements in the bottom sediments on different banks of the Sheksninsky spur were not revealed, since the p values for most elements were higher than 0.050, except for lead, where p=0.042 (Table.1), which shows significant differences in the lead content in bottom sediments on different coasts. According to the results obtained, it can be assumed that the different hydrological regime and other factors affecting the Sheksninsky spur did not create significant differences affecting the accumulation of heavy metals in the study period.

Table 1. Results of the nonparametric Mann-Whitney U-test for the content of heavy metals in the bottom sediments of the Sheksninsky spur of the Rybinsk reservoir

variable	Mann-Whitney U-test (with continuity correction)				
	The observed correlations are significant at the level of $p < 0.05000$				
	the total rank of the right	the total rank of the left	p-level.	Z corrected	2-way accurate p
Pb	109.000	62.000	0.042	2.030	0.039
Zn	56.000	80.000	0.750	-0.317	0.757
Cu	91.000	80.000	0.658	0.441	0.666
Cd	17.000	38.000	0.150	1.436	0.177
Mn	66.000	105.000	0.093	-1.677	0.093
Fe	54.000	82.000	0.596	-0.529	0.606
Hg	68.000	103.000	0.133	-1.501	0.135

To identify the absence or presence of a correlation between the heavy metal contents, the pair correlation matrices were constructed (Tables 2, 3). When establishing the dependencies, the nonparametric Spearman coefficient was used.

Table 2. Correlation of heavy metals, organic matter in the sediments of the right Bank of the Sheksna Cherepovets

variable	Pb	Zn	Cu	Cd	Mn	Fe	Hg	organics
Pb	1.00	-0.07	-0.17	-0.66	0.51	0.86	-0.58	-0.50
Zn	-0.07	1.00	0.79	0.05	-0.19	-0.004	0.74	0.45
Cu	-0.17	0.79	1.00	-0.10	-0.18	0.04	0.71	0.32
Cd	-0.66	0.05	-0.10	1.00	-0.84	-0.91	0.47	0.49

Mn	0.51	-0.19	-0.18	-0.84	1.00	0.72	-0.51	-0.60
Fe	0.86	-0.004	0.04	-0.91	0.72	1.00	-0.57	-0.58
Hg	-0.58	0.74	0.71	0.47	-0.51	-0.57	1.00	0.70
organics	-0.50	0.45	0.32	0.49	-0.60	-0.58	0.70	1.00

According to the results of the correlation analysis, direct strong dependencies were revealed: Pb-Fe, Zn-Cu-Hg, Cu-Hg, Mn-Fe, Hg – organic matter.

The revealed dependencies show that the increase or decrease in the content of some elements changes along with the content of others. When the zinc content increases, the values of copper and mercury increase.

The sorption of mercury by organic matter plays a greater role than the sorption of other elements, the correlation is significant $r=0.70$ [15].

The significant relationship of Mn-Fe indicates the possible occurrence of iron-manganese nodules, they occur in reservoirs with a large amount of organic acids. Zinc and copper are interrelated because they belong to the same group of elements, namely, lithophilic elements. The Zn – Hg bond is caused by the fact that these elements belong to the same group of chalcophilic elements [16, 17]. In the accumulation of heavy metals, the role of organic matter is insignificant, except for mercury, its accumulation is interrelated with the content of organic substances. Inverse strong dependencies show a strong relationship in the content of elements, but if the number of one element increases, the number of related elements decreases in direct proportion. The Cd – Mn – Fe inverse relationship was revealed.

Table 3. Correlation of heavy metals, organic matter in the sediments of the left Bank of the Sheksna Cherepovets

variable	Pb	Zn	Cu	Cd	Mn	Fe	Hg	organics
Pb	1.00	0.42	0.29	-0.10	0.39	0.81	-0.69	-0.06
Zn	0.42	1.00	0.62	-0.13	0.62	0.45	-0.11	0.18
Cu	0.29	0.62	1.00	0.000	0.28	-0.009	-0.10	-0.06
Cd	-0.10	-0.13	0.000	1.00	-0.44	-0.13	0.34	-0.14
Mn	0.39	0.62	0.28	-0.44	1.00	0.55	-0.29	-0.22
Fe	0.81	0.45	-0.009	-0.13	0.55	1.00	-0.60	-0.25
Hg	-0.69	-0.11	-0.10	0.34	-0.29	-0.60	1.00	0.35
organics	-0.06	0.18	-0.06	-0.14	-0.22	-0.25	0.35	1.00

According to the results of the correlation analysis of the gross content of heavy metals in the bottom sediments of the shallow zone of the Sheksna River on the right bank, a direct strong relationship between the elements was revealed: Pb-Fe and a strong inverse relationship [Pb-Fe] - Hg. The amount of iron and lead depends on the mercury content in the samples. The strong correlation between the metals indicates that the heavy metals

share a common geochemical behavior and come from similar pollution sources [13]. The lack of correlation between heavy metals indicates that the content of these metals is not controlled by a single factor. The role of organic matter in the accumulation of heavy metals in bottom sediments of the shallow waters of the Sheksninsky spur is insignificant. The maximum accumulation of heavy metals for Rybinsk reservoir is observed in bottom sediments of Sheksninsky ples [14]. The main source of heavy metals in the natural waters of the studied water body are wastewater from chemical enterprises (AO "Apatite"), metallurgical industry (PAO "Severstal"), agricultural runoff, roads along the banks. Also in the study area there are berths OAO "Cherepovets Port" and OAO "Severstal-Invest" (engaged in metal rolling and metalware) and OAO "Cherepovets Shipbuilding and Ship Repair Plant" [12]. Water is very important in the formation of bottom sediments. Contaminants entering water bodies redistribute relatively quickly between water and bottom sediments, then they are partially inactivated, interacting with each other or forming new compounds, possibly more toxic than the original ones [2]. Of particular importance for the formation of water and bottom sediments of the Sheksna spur is the heavily polluted river Yagorba (polluted by runoff of AO "Cherepovets match factory "FESKO", OAO "Cherepovets Shipbuilding and Ship Repair Plant"), livestock complex (Pork complex ZAO "Botovo") and cottage villages) which flows into the Sheksna on the study area. Discharges of pollutants in Yagorba exceed 38 thousand tons per year [11, 14]. Specific combinatorial water pollution index value for Sheksna river was 4A (dirty) [14], there were exceedances of Fe (3.3 MPC), Cu (2.1 MPC), Zn (2.3 MPC), Mn (5.4 MPC). These facts cannot but affect the formation of the qualitative and quantitative composition of bottom sediments of the Sheksna spur. The qualitative composition of bottom sediments is the most important factor in the state of the environment.

In the course of the correlation analysis, the dependence of the metal content in the bottom sediments on the water temperature was also studied, but no dependence was found, which may indicate the influence of other biotic, abiotic and anthropogenic factors on the accumulation of elements.

Thus, according to the results of the correlation analysis, a greater number of dependencies with heavy metals were revealed on the right bank, which may be due to its lower pollution compared to the left bank, which is confirmed by the literature data [17]. Based on the results of the metal content in the bottom sediments, it can be assumed that the different hydrological regime and other factors (temperature, humidity, organic matter, etc.) that affect the Sheksninsky spur did not create significant differences affecting the accumulation of heavy metals in the study period. It may be determined by different types of soils in the bottom sediments of the left bank (mostly sand and sandy silt) and the right bank (sand), the slope of the channel (the left bank is flatter, has many pools), flow rate (the right bank has an intensive longshore movement of water masses because of waterway) and intensity of surface and underground flows in different time periods, processes of sorption and desorption of metals on the surface of bottom sediments and physical and chemical properties of elements themselves.

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