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Migration of heavy metals in water ecosystems (using the example of the Belaya River in the North-Western Caucasus)

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The results of the study of the content, spatial distribution and transformation of Fe, Mn, Pb, Zn and Cu in the system of benthal deposits of the Belaya River are presented. The results obtained were compared with the background concentrations of metals, which allow us to estimate the anthropogenic component. It has been established that discharges from industries cause increased concentrations of metals in benthal deposits in certain areas of the Belaya River basin.

Keywords: Organic substances, heavy metals, water bodies, ecosystem, bottom sediments, transformation, adsorption capacity, hydrochemical factors.

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1 Introduction

Currently, methods for assessing water quality using the MPC system of pollutants do not give a complete picture of the state of natural waters and are not a sufficient guarantee of their protection from pollution. When assessing the level of pollution of the river, the average annual concentrations of pollutants in the water flow are used. To obtain objective annual averages, it is necessary to select and analyze a large number of samples taken in different hydrological periods of the year. The ratio of suspended and dissolved forms of heavy metals plays an important role. According to the generalized data of such studies made by *Strakhov et al.* [1954], *Lisitsyn* [1956], *Demina* [1982], *Moore and Ramamurti* [1987] and *Balls* [1989], the predominance of the suspended form over the dissolved one is observed for most trace minerals in river ecosystems. As benthal deposits are the most conservative component of the river ecosystem, reflecting the level of heavy metals in the water column of the river, so they can act as an objective source of information about the degree of pollution of the water system as a whole.

It follows from the numerous published data that the mineralogical composition and grain size characteristics of benthal deposits control the change in heavy metals in them *Potemkin* [1967], *Moore and Ramamoorthy* [1984]. Therefore, when assessing the level of pollution of benthal deposits, it is necessary to take into account the influence of these factors and introduce appropriate amendments. Regulatory actions are a widely used technique in practice for leveling differences in an emerging the formation of benthal deposits. It is known that various regulatory actions are used in this case: on the content of fine fractions (< 20 microns) in the composition of benthal deposits [*Demina*, 1982]; on the content of carbonates, C_{org} and Al_2O_3 [*Melnichuk*, 1993]; calculation of the concentration coefficient relative to silicon [*Lisitsyn*, 1956], relative to aluminum and lithium [*Mizandrontsev*, 1990], relative to iron [*Bok*, 1984]. It is assumed that there is a linear relationship between the elements, i.e. the concentration of the indicator element varies depending on the mineralogical composition and grain size characteristics of the bental deposits, and thus the concentration of the regulated element changes proportionally. Therefore, the regulated element should be

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an important component of one (or more) carrier of heavy metals and reflect the grain size variability of benthal deposits.

The degree of influence of iron hydroxide and manganese oxide on the sorption of metals is much greater than would be expected based on their weight contribution in the composition of sediment particles. This is due to the ability of these natural sorbents to cover the surface of other solid sediment particles with a thin layer, which significantly increases their specific working sorption area. Based on this, it can be assumed that the concentration of iron and manganese can be used as a regulating factor when comparing the content of heavy metals in benthal deposits and suspended solid of rivers. Statistical processing of the results (regression dependencies and regulation) is presented in the works of: *Gibbs* [1977]; *Luoma and Bryan* [1981]; *Groot et al.* [1982]; *Leinen and Pisias* [1984] and experimental and mathematical modeling in the works of: *Jenne* [1995]; *Petersen et al.* [1995]; *Moran et al.* [1996]; *Huang et al.* [1996]; *Turner* [1996]; *Widerlund* [1996].

The aim of the work is to study the spatial distribution and accumulation of heavy metals in the benthal deposits at various sectors of the Belaya River.

2 Object of study and methods

The Belaya River is the second longest and most powerful left-bank tributary of the Kuban River, flowing into the Krasnodar reservoir. The catch basin covers an area of 5990 km^2, the length of the river's watercourse is 277 km. The River has its source at the peaks of the Main Caucasian Ridge at an altitude of 2197 m above sea level. The river basin is elongated in the meridian direction and has an asymmetric structure of the river system. It takes mainly left-bank tributaries in the middle and lower reaches and right-bank ones only on the upper reaches of the River. Seven monitoring sections have been tested on the Belaya River, samples of benthal depodits were taken by Peterson D-25 dredge at a depth of 10 cm from the surface of the occurrence. After being sieved by nylon sieves, the samples were divided into two particle size fractions with a cell diameter of 1.0 to 0.25 mm and < 0.25 mm and decomposed with a mixture of HNO_3 acids: H_2SO_4: HCl : H_2O_2 = 2 : 1 : 1 : 2 at low heating [*Alekseenko*, 2000]. Background concentrations of heavy metals were determined at a depth of 20–30 cm. The study also identified hydrochemical parameters: pH, ox-redox potential and organic carbon.

Determination of the concentration of heavy metals (Pb, Cu, Fe, Mn and Zn) in benthal deposits was carried out by atomic absorption method in the laboratory of the Federal State Institution "Center of Hygiene and Epidemiology in the Republic of Adygea" on the spectrometer "QUANT-AFA". The measurements were carried out in 3-fold repetition. The relative error is within 0.01–5%.

3 Results and discussion

The content of all metals in the studied samples is at the background level, with the exception of only individual sampling intake points, where the content of Pb, Zn and Cu slightly exceeds the background level. The maximum values of Zn concentrations in benthal deposits were recorded on the sections of villages Ministochnik and Bzhedughabl and at the mouth of the Belaya River, Pb – at the intake points of Ministochnik village and at the mouth of the River, Cu – in the lower reaches of the Belaya River.

The content of the studied metals in benthal deposits is significantly higher than in water. In terms of concentrations, metals are arranged in the following decreasing series: Fe > Mn > Zn > Pb > Cu (Table 1). The system "benthal deposits – bottom water" is quite complex and its main determining factors are redox processes, the presence of complexing agents, pH, temperature, etc. Higher pH values and the ox-redox potential of the bottom layers of water make it difficult for metals to pass from sediments into the water column. The latter confirms the accumulating role of benthal deposits and the conclusion that the migration of heavy metals in the Belaya River in the "water – benthal deposits" system goes from top to bottom.

According to many authors, pH medium and the sulfate-sulfide equilibrium, which, in turn, is determined by the redox conditions of the benthal deposits, have a decisive influence on the occurrence form and the level of metal content in benthal deposits and suspended solids [*Demina*, 1982; *Lisitsyn*, 1956; *Melnichuk*, 1993; *Mizandrontsev*, 1990; *Horowitz*, 1985; *Steell and Wagner*, 1975; *Vasiliev et al.*, 1990]. A change in redox conditions in benthal deposits leads to a change in the valence of metals and the occurrence form for natural waters of any type, regardless of their chemical composition or hydrological regime. On the basis of the results obtained, it can be stated that metals in almost all the studied intake points are concentrated in the benthal deposits of the river in the oxidative horizon in poorly soluble forms and associated with organic matter. Metals are present in the form of carbonates with a transition to sulfide forms on sectors of the River near the villages of Ministochnik, Khanskaya and Adamiy.

It is known that under anaerobic conditions sulfide anions are formed in benthal deposits *Sa-*

Table 1: The content of heavy metals in the benthal deposits of the Belaya River, mg/kg dry weight

Element	fraction, mm	intake point number							C_v,%
pH	—	7.51	7.52	7.53	7.54	7.95	8.27	8.30	—
Eh	—	+ 229	+ 346	+ 49	+ 179	+ 61	+ 191	+ 167	—
Cu	1–0.25	6.576	5.189	4.578	2.688	5.632	5.729	5.226	3.73
	< 0.25	5.104	4.041	5.945	2.331	6.287	6.778	6.076	3.77
	background	3.67	3.86	3.06	2.57	4.95	3.15	4.97	3.76
Zn	1–0.25	9.564	10.025	12.509	4.371	9.146	9.983	10.407	4.10
	< 0.25	10.306	9.570	14.983	4.228	11.520	13.317	11.415	4.11
	background	8.16	10.08	7.28	4.87	9.74	6.80	8.99	4.06
Pb	1–0.25	9.266	9.911	11.713	7.176	4.222	3.996	5.021	4.25
	< 0.25	9.632	9.347	12.891	6.423	4.345	5.038	4.901	4.24
	background	10.57	10.09	8.32	5.46	4.16	2.67	3.53	4.24
Fe	1–0.25	727.71	700.44	691.31	380.06	1699.99	1869.0	1870.5	25.0
	< 0.25	704.28	711.94	723.21	356.68	1822.67	2096.4	1983.6	25.0
	background	745.00	714.60	640.37	349.65	1721.60	1524.9	2047.5	25.0
Mn	1–0.25	112.86	101.10	67.97	53.097	91.67	96.01	98.97	25.0
	< 0.25	57.83	106.32	64.67	60.48	88.14	98.29	101.08	25.0
	background	74.19	106.99	45.63	56.12	84.79	62.39	110.14	24.9
$C_{org.}$, %	1–0.25	19.33	23.17	22.82	83.83	16.65	99.54	23.05	—
	< 0.25	16.42	22.82	22.59	14.09	13.86	49.49	19.44	—

Note: the confidence interval at P = 0.95 was (%): Fe – 8–45, Mn – 12–25, Cu – 7–25, Zn – 16–55, Pb – 16–50.

lomons and Forstner [1984], *Di Toro et al.* [1992], *Melnichuk* [1993], *Alekseenko* [2000].

Under anaerobic conditions in the surface layer of benthal deposits, iron (III) hydroxide is reduced to soluble iron (II) hydroxide and manganese (IV) oxide – to manganese (II) while heavy metals of MnO_2 and $Fe(OH)_3$after being sorbed on the surface of the loose structure are released into the pore water. Poorly soluble metal sulfides are formed in the presence of sulfide ions (S^{2-}) in pore water, which are once again precipitated in benthal deposits [*Tretyakova*, 2000; *Di Toro et al.*, 1992].

With the process of entering heavy metals in benthal deposits under anaerobic conditions and we noticed that the content of organic carbon increases on average by an order of magnitude in the large fraction over the small fraction under aerobic and moderately anaerobic conditions in the benthal deposits of the Belaya River.

The comparative sampling of benthal deposits with grain size separation of fractions has showed: significant changes in the content of Fe in three of the seven intake points (Khanskaya village – Adamiy village), the high reliability of differences in the content of Pb in five of the seven intake points (Ministochnik village – Adamiy village). The content of Zn in the sections of the villages Ministochnik and Bzhedughable determined the high reliability of the results and the content of Cu – in the sections of the villages Dakhovskaya and Adamiy. It follows from the results that the samples are almost homogeneous in the studied intake points.

One of the most important factors affecting the adsorption capacity of heavy metal ions is the particle size. The surface area of the particles is of decisive importance [*Bok*, 1984]. Statistical analysis of the relationship of metal concentrations with the particle sizes of the benthal deposits of the Belaya River showed that the correlation coefficients have positive values for particles with sizes of 0.25–1.0, < 0.25 mm. The heavy metals that are well absorbed are: Fe (r = 0.99), Pb (r = 0.97), Cu (r = 0.69), Zn (r = 0.93), Mn (r = 0.45). This means that silt particles are the main sorbing and coagulating material for the heavy metals listed above.

A significant role of Fe and Mn in the geochemical cycles has been repeatedly mentioned in the literature. The processes of circulation of a number of chemical elements between water and benthal deposits are associated with oxides and hydroxides of iron and manganese that are good adsorbents of elements from aqueous solutions, due to high negative charge values, large surface area of particles and high cation exchange capacity [*Mizandrontsev*, 1990]. The research data indicate an average correlation of Fe with concentrations of Cu (r = 0.48), Mn (r = 0.44), Zn (r = 0.32), Pb (r = –0.81). The maximum values of these coefficients are noted for particles with a diameter of < 0.25 mm: r = 0.79 (Cu), r = 0.65 (Mn), r = 0.50 (Zn), Pb (r = –0.70).

The Mn concentration for the fraction of particles with a diameter of 0.25–1.0 mm is closely related to the concentrations of Cu (r = 0.92), Zn (r = 0.45) and Pb (r = −0.18) and for the fine fraction the corresponding indicators are 0.37 (Cu), 0.25 (Zn) and – 0.47 (Pb). The highest correlation coefficients of the Fe content with the above-mentioned metals are characteristic of the small fraction, while Mn is a characteristic of the larger fraction, which indicates the identity of the transformation processes of heavy metals in benthal deposits. The obtained high values of the correlation coefficients of Mn and Fe content with Zn and Cu concentrations indicate the participation of these elements in the Fe and Mn redox cycle.

The analysis of the obtained correlation matrix showed that there is no strong correlation between the studied indicators. The dependence between the indicators, apparently, indicates the nonlinearity of the links between them.

4 Conclusion

The content of heavy metals in the benthal deposits of the Belaya River, in general, is at the background level for uncontaminated reservoirs. Heavy metals in the benthal deposits of the same intake point are distributed unevenly, and there is a significant spatial variability. At the time of the study, the migration of metals in the "water – benthal deposits" system goes mainly from top to bottom.

The priority hydrochemical factors affecting the content of heavy metals in the benthal deposits of the Belaya River are redox conditions. The accumulation of heavy metals and organic substances in the sediments of the studied areas of the Belaya River are taking place in parallel. The highest correlation coefficients of the Fe content with the studied metals are characteristic of the small fraction, while Mn is characteristic of the larger fraction, which indicates the identity of the transformation processes of heavy metals in benthal deposits.

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