Spatial Distribution of the Content of Heavy Metals in the Belaya River Ecosystem

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Abstract
This paper presents the results of the research on the content and spatial distribution of heavy metals in the system of “water – bottom sediments” of the Belaya River. Quantitative data were obtained and the authors performed comparative analysis of the pollution of various abiotic environments of the river ecosystem. The pattern of vertical distribution of heavy metals in bottom sediments is shown to be linked to the level of pollution and conditions of the river flowage. Concentration of dissolved and suspended forms of the studied elements (the content of Fe, Mn, Cu, Pb, Zn, the oxidation-reduction potential, pH, turbidity and water temperature) in water samples from different gauge stations of the Belaya River is characterized by heterogeneity. There is a clear tendency for the increase of the content of Fe, Mn, Zn, and Cu down the river flow with the maximum concentrations in the foothill zone of the Republic. The studied heavy metals have prevalence of the suspended form of migration. Concentration of heavy metals in bottom sediments is considerably uneven in their distribution in different sites of the Belaya River. Bottom sediments are noticeably polluted with Zn and Pb at the village of Ministochnik, the aul of Bzhedugkhabl, and at the river mouth. In the lower watercourse of the Belaya River, contamination of bottom sediments with Cu prevails. In the gauge stations with low content of heavy metals, their vertical distribution is quite homogenous. In less polluted parts of the river, flowage plays an important role in vertical distribution of heavy metals. For example, with weak flowage (the part of the river from the village of Ministochnik to the aul of Bzhedugkhabl), the highest concentrations are in the surface layers of 0–10 cm in comparison to the layer of 10–30 cm. With strong flowage (Dakhovskaya stanitsa), the lowest content of heavy metals is in the upper layer of 0–10 cm, and the highest is in the layer of 10–30 cm.

Key words: Republic of Adygeya, Belaya River, heavy metals, bottom sediments, suspended matter.

Introduction

In recent years, the geosystems of the river basin have been given increased attention as functional-holistic territorial systems (Tkachev & Bulatov 2002). Their integrity is determined by the movement of the water flow, and the entry of chemical elements and solid matter into it. Economic development of the territories of the river basins significantly changes flows of substances, which, in turn, affects the condition of natural and natural-anthropogenic landscapes and human economic activities (Khublaryan 1994). In this regard, basins of small and average reservoirs can be considered as local ecosystems.
When estimating the condition of a local ecosystem of a water object, it is important to consider its contamination with toxic substances. Heavy metals constitute the greatest danger. In certain concentrations, they not only influence the quality of fresh water, but also become toxic for hydrobionts (organisms, constantly living in the water environment) accumulating in their tissues. Heavy metals may penetrate into human bodies through trophic chains. This therefore dictates the need for the research on contamination of local ecosystems of water objects with heavy metals (Gapeeva et al. 1997; Orlov et al. 2002; Fischer 1979; Plant 1983).

The basin of the Belaya River (the left tributary of the Kuban River) is a complex natural and anthropogenic system with interactions of natural, urbanized and agrarian landscapes. On the banks of the Belaya River, which is the main waterway of the Republic of Adygeya, there are a large number of big and mid-sized settlements with a quite developed network of agricultural and industrial enterprises. Therefore, contamination of the Belaya River with heavy metals (Zn, Cu, Pb) is one of its problems. In scientific literature, there is no quantitative assessment of anthropogenic and natural factors defining the source of heavy metals getting into a river network, there are no data of physical or chemical indicators on interphase distribution of substances in the system “water – bottom sediments”. This results in considerable difficulties in the analysis of available information, difficulties in obtaining objective data on the sources of heavy metals, on the extent of pollution of various sites of a river, primary data for operational monitoring and long-term forecasting.

Figure 1. Location of gauge stations in the Belaya River basin.

The Belaya River is the second longest and the most powerful by water content left tributary of the Kuban River falling into the Krasnodar reservoir. The catchment basin has the area of 5990 km², the river waterway
length is 277 km. The river originates at the tops of the Greater Caucasus Range at the height of 2197 m above sea level. The river basin is extended in the meridian direction and has an asymmetric structure of the river system: it has mostly left-bank tributaries in the middle and lower course and right-bank tributaries only in the upstream. The right-bank tributaries are the Keesha River and the Dakh River, 52 km and 23 km long, respectively, joining the river in the upstream. The area of their catchment basins is 499 km$^2$ and 389 km$^2$ respectively. The main left-bank tributary is the Pshekha River 139 km long, located lower than Belorechensk. The area of its catchment basin is 2090 km$^2$ (Fig. 1).

The water regime of the Belaya River is formed by glacial and snow supply, ground water, and rainfall. The river speed is very diverse, and subject to change depending on the season, water volume, and on the location of a specific gauge station (Kupriyanov 1973).

Material and Methods

Assessment of the ecological condition of the Belaya river basin was carried out by fieldwork with sampling of water and bottom sediments in seven gauge stations (Fig. 1). The samples were tested for the presence of Zn, Cu, Mn, Pb, Fe and hydrochemical indicators – organic carbon, pH, the oxidation-reduction potential (Eh), turbidity, and water temperature (Aleklin et al. 1973; Semenov 1977).

Selection and preparation of the samples for analysis were made according to the generally accepted techniques and standards (Bock 1979; GOST 17.1.5.01-80; GOST 17.1.5.01-85; GOST P 51592-2000; ISO 5667/3:2012; ISO 5667/4:2016). Bottom sediments were decomposed by the mix of acids HNO$_3$:H$_2$SO$_4$:HCl:H$_2$O$_2$ = 2:1:1:2 (to define mobile forms of heavy metals). Quantitative determination of the content of heavy metals in the samples (water and bottom sediments) was made by the nuclear and absorbing method on AA – spectrometers “Quantum – ZETA” and “Quantum – AFA”. Determination of pH and the oxidation-reduction potential was made by the potentiometric method on the “Ionnomer I — 130” device. The value of organic carbon ($C_{org}$) was determined by the Tyurin wet combustion method (Arinushkina, 1970).

Data from the fieldwork were statistically analysed: correlation coefficients and confidence limits of parameter variations for the 0.95 probability were determined.

Results

Screening research on the content of heavy metals in the water flow allows estimating the level of the river pollution in different places, as well as tracking spatial distribution and revealing sources of heavy metals in the riverbed.

Content of Heavy Metals in Water

Concentration of heavy metals in the bottom water slightly increases closer to the estuarial zone of the Belaya River. It was established that the elements can be put in the following order according to the concentration level: Fe (0.19–2.7 mg/dm$^3$) > Mn (0.007–0.22 mg/dm$^3$) > Cu (0.0009–0.14 mg/dm$^3$) > Zn (0.0013–0.043 mg/dm$^3$) > Pb (0.00008–0.0025 mg/dm$^3$).

Average concentration of dissolved forms of heavy metals in the surface water exceeds the maximum permissible concentration (MPC) in Fe for general-purpose water and amounts to 1.1–5.2 of MPC. The excess of Mn is insignificant. Comparison of the results with a stricter standard for fishery reservoirs (List..., 1999) allowed establishing the variability range of content concentration values: from 1.2 to 27.0 of MPC for Fe (on average, 8–13 of MPC), from 0.7 to 31 of MPC for Mn (on average, 1.2–11 of MPC). Concentration of dissolved forms of zinc is noted only in spring and amounts to 1.3–2.1 of MPC on average.

Analysis of the selected samples for the content of heavy metals in the bottom water of the Belaya River has revealed significant differences in the samples of the control gauge stations in relation to the natural background (gauge I). According to the Student’s t-test, there are significant differences in three of seven gauges by the content of Fe (gauge II – t=2.54, gauge IV – t=2.24 and gauge V – t=2.73) and by the content of Mn – in four of seven gauges (significant differences in gauge II – t=3.30 and gauge III – t=2.20; highly significant in gauge V – t=4.49 and close to significance in gauge VI – t=1.96).

To establish links between heavy metals, pH and oxidation-reduction conditions, correlation coefficients were defined for different seasons. In spring, there is a correlation between the indicators of
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oxidation-reduction reactions and Zn and Cu content ($r=0.66–0.69$) and a very high correlation between Zn and Mn content ($r=0.85$). The relationship between iron and manganese is characterized by the average value, with the correlation coefficient of 0.52. In autumn, the highest correlation is noted between Pb, Fe, Cu ($r=0.69–0.73$).

Content of Heavy Metals in Suspended Matter
The average-weighted concentrations of heavy metals in the suspended matter throughout the Belaya River change within a wide range: Fe – from 3.1 to 2287.3 mg/kg, Mn – from 0.75 to 64.5 mg/kg, Pb – from 0.08 to 115.1 mg/kg, Cu – from 0.24 to 0.7 mg/kg, and Zn from 1.4 to 15.8 mg/kg. The highest concentration of heavy metals is in the middle watercourse due to rainfall flow. During autumn homothermy (uniformity of water temperature in the reservoir depth) in the lower watercourse there is some increase in the content of heavy metals in suspended matter. This is indicative of desorption and ionic exchange on the surface of suspended matter. This results in transformation of some Fe, Mn and Zn into the dissolved form, and adsorption of Cu and Pb on the surface of suspended matter.

Increase in the quantity of transported deposits in the spring high water period and in autumn results in overwhelming prevalence of suspended forms of heavy metals in the water. Percentage of dissolved forms of heavy metals in spring and autumn is respectively as follows: Fe – 0.1–17% and 0.5–73.5%; Mn – 0.06–17.4% and 0.2–73.4%; Pb – 0.04–7.7% and 0.1–14.8%; Zn – 0.17–8.14% and 89–99.3%.

For the analysis of the condition of water ecosystems, it is preferable to compare the number of suspended particles of heavy metals in a litre of water and their specific concentration in the suspended matter (Linnik & Timchenko 1986; Balls 1989). If both parameters show increased concentration, then it is possible to confirm with certainty the existence of the source of this metal in the studied part of the river. In the Belaya River, such situation was noted 3–5 km below the zone of operation of the Maykop field of geothermal waters and agricultural enterprises (as regards to the content of Pb, Zn and Fe), and 1 km below Maykop to the rivermouth in the zones of urbanized and agrarian landscapes (as regards to the content of Fe, Mn, Pb, Cu and Zn). Analysis of spatial distribution of heavy metals in suspended matter in the zones of industrial and agricultural enterprises showed a tendency to accumulate most of heavy metals not near the object (pollution source), but at a certain distance from it (1–3 km).

Content of Heavy Metals in Bottom Sediments
Concentration of heavy metals in river bottom sediments usually exceeds their concentration in the water column (Denisova et al. 1987; Forstner 1993). Bottom sediments in the middle course of the Belaya River are represented by gravely-pebbly alluvium with sandy filling, in the lower course – by covered clay and silt sediment. Analysis of the dynamics of mobile forms of the studied heavy metals in river bottom sediments has shown that the average content of elements varies by year and season. However, yearly variations of concentration of heavy metals are much lower than seasonal ones. The content of heavy metals in the top layer of bottom sediments considerably varies: Zn – from 2.6 to 33.2 mg/kg (on average, 11.3 mg/kg per year); Pb – from 1.1 to 14.8 mg/kg (on average, 4.9 mg/kg per year); Cu – from 0.5 to 7.5 mg/kg (on average, 3.7 mg/kg per year); Mn – from 25.1 to 140.7 mg/kg (on average, 73.1 mg/kg per year); Fe – from 276.0 to 2217.3 mg/kg (on average, 1172.8 mg/kg per year).

Many authors note that the content of heavy metals in bottom sediments depends on many factors. The environmental pH and the sulphate-sulphidic balance considerably influence occurrence forms and the level of content of heavy metals. The balance is determined by oxidation-reduction conditions of bottom sediments (Horowitz, 1985; Forstner 1990, 1993; Steell & Wagner 1975). According to Salomons & Stigliani (1995), change of these conditions in bottom sediments has two main consequences. First, valence of metals changes, and, second, occurrence forms change (occurrence of heavy metals in poorly soluble or easily soluble forms). At the same time, the influence of oxidation-reduction conditions of bottom sediments on occurrence forms of heavy metals has the same nature for natural waters of any type, irrespective of their chemical composition or hydrological regime (Linnik, Nabivanet, 1987; Tretyakova & Papina 2000; Wood, 1987; Yeats & Loring 1991).

The gradient of change of oxidation-reduction conditions and pH value, as well as concentration of dissolved organic matter, are the most typical driving forces of intensification of exchange of heavy metals in the system “bottom sediments – pore solution” in river bottom sediments (Forstner, 1995; Zubkova 1996). The hydrogen indicator (pH) of bottom sediments of the Belaya River changes from 7.51 to 8.41 with an
average pH value of 7.98. The content of organic carbon in bottom sediments in the downstream increases, and amounts to 19.92% and 45.74% in the upstream and downstream, respectively.

Oxidation-reduction processes in the diagenesis of bottom sediments cause redistribution of chemical elements coming with suspended matter in the process of sedimentation. In the top layer of bottom sediments, in spring, the oxidation-reduction potential (Eh) is +49 – +346 mV. During the vegetative period, the oxidation-reduction potential indicates the emergence of reducing conditions and reaches more than +163 mV.

To detect statistical relationships between the defined indicators, paired correlation coefficients between indicators of pollution of bottom sediments and physical and chemical indicators have been calculated.

Valuation of Concentration of Heavy Metals in the Suspended Matter and Bottom Sediments by Mn and Fe

Modern methods of water quality assessment by the system of MPC of polluting substances do not provide a complete understanding about the condition of the river water. When assessing river pollution, it is more correct to use average annual concentrations of polluting substances in a water flow.

In order to obtain objective average annual values, it is necessary to select and analyze a large number of samples taken in different hydrological periods of a year. Bottom sediments are the most conservative component of a river ecosystem reflecting the level of the content of heavy metals in the water column. Therefore, they can act as an objective source of information on the extent of water system pollution in general.

The method, developed by the authors, allows revealing sources of heavy metals, estimating environmental pressure of heavy metals both on specific sites and on the river ecosystem in general, as well as assessing environmental pressure on river ecosystems in remote areas where creation of environmental monitoring stations is impossible.

Mineralogical composition and granulometric characteristics of bottom sediments affect the content of heavy metals (Potemkin 1967; Moore, 1984; Linnik & Nabivanets 1987). Concentration of the indicator element changes depending on mineralogical composition and granulometric characteristics of bottom sediments, and at the same time, concentration of the normalized element proportionally changes. Therefore, the normalizing element must be an important component of one (or more) carrier of heavy metals and reflect granulometric variability of bottom sediments. We find it necessary to take into account the impact of these factors in the assessment of pollution of river sediments and to introduce related amendments.

In water, many heavy metals actively connect with amorphous hydroxides of Fe and Mn, as they are good natural sorbents of the studied set of heavy metals. This leads to the assumption that it is possible to use concentrations of Fe and Mn as a normalizing factor in the comparison of the content of heavy metals in bottom sediments and in the suspended matter in rivers.

All the sampling gauge stations revealed correlation between the content of Fe and studied heavy metals in spring and autumn (r=0.32–0.80, r=0.56–0.96, respectively) and between the content of Mn and other heavy metals (r=0.25–0.92, r=0.26–0.87, respectively).

Cluster analysis has shown that the indicator component reflects the influence of fraction dimensions on the content of heavy metals in bottom sediments. Moreover, variations of concentrations of heavy metals in different sites of the river (except for the mouth) are primarily caused by the change in the content of fractions of bottom sediments of 1.0–0.25 mm (sand of various fineness).

According to the research of Salomons & Forstner (1984), Di Toro et al. (1992), Melnichuk (1993) and Tretyakova & Papina (2000), the flow of heavy metals and organic carbon into bottom sediments prevails under anaerobic conditions in a fine granulometric fraction. Our research, however, has not confirmed this mechanism.

The largest accumulation of heavy metals and organic carbon is observed in a coarse granulometric fraction of bottom sediments under aerobic and moderate anaerobic conditions. The results of the research show that accumulation of heavy metals and organic matter in bottom sediments of the studied sites of the Belaya River occurs through two concurrent processes. The high content of heavy metals under anaerobic conditions is linked to formation and sedimentation of insoluble sulphides of heavy metals in bottom sediments. Sharp speed reduction in organic matter destruction under reducing conditions leads to accumulation of organic carbon.

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Discussion

The results of the research in the Belaya River basin show that there is a clear seasonal distribution of heavy metals in dissolved and weighted forms. In general, heavy metals are concentrated in suspended matter. The exceptions to this in autumn are gauge stations I–IV by the content of Fe, gauges II–III – by the content of Mn; gauge III – by the content of Pb. Zinc migrates mainly in the dissolved form.

Excess of Fe and Mn according to the standards for fishery reservoirs has been found in all the river sites. However, the highest concentrations are in the middle watercourse, namely near Maykop (gauge IV). The deposit of iron-manganese ores in the interbed of bioherms of the Early Sarmatian (the ore formation of the ancient sea basin) can be considered the reason for such situation.

Average concentrations of heavy metals in the water considerably increase in the river flow after the settlements: Ministochnik village (gauge III), city of Maykop (gauge IV) and Bzhedugkhabl aul (gauge VI). The revealed spatial dynamics of the content of heavy metals in the river system is probably caused by their sources in the studied sites.

The results of the research have shown that in water heavy metals prevail as part of the suspended matter. This is caused by chemical properties of these metals, ions of which are actively sorbed by natural sorbents. Analysis of the samples for the content of heavy metals in suspended matter in the studied sites of the Belaya River has revealed a strong positive relationship between the content of Cu and Mn, Cu and Zn (r=0.68–0.95).

Relationship between the indicators of water turbidity, acidity and concentration of heavy metals is poor and very poor (r=0.08–0.36). This is because suspended matter of smaller fractions has high sorption capacity. Under the conditions of high speeds of the river flow, suspended matter stays in the stream flow for a long time and plays a major role in interphase distribution of heavy metals in the “water – suspended matter” system.

The results have shown that heavy metals in almost all gauge stations concentrate in bottom sediments of the Belaya River in the oxidizing horizon in poorly soluble forms. Around gauges III and IV, heavy metals are present in the form of carbonates with transition to sulphidic forms.

The largest amount of mobile Mn, Pb and Cu in bottom sediments is observed in spring. In autumn, with its intensive biological circulation, there is essential decrease in Fe and Zn concentrations. This is caused by mixing of water masses (homothermy), accompanied by oxidation of heavy metals and their sedimentation in the form of hydroxides (Fe(OH)_3 и Zn(OH)_2) (Nordberg et al. 2007).

The results of the research have demonstrated a direct relationship between the contents of Zn and Mn (r=0.76) and a very strong relationship between the contents of Zn and Cu (r=0.90). The negative relationship between the pH value and the contents of Mn, Pb, Zn, and Cu is much weaker, which confirms their higher mobility in the acidic environment (Mizandrontsev 1990). The relationship between the oxidation-reduction potential and such metals as Mn and Zn is strong – 0.88 and 0.69, respectively. The relationship between the concentration of Fe and organic carbon is average (r=0.56).

There is a positive association between the concentrations of heavy metals and the oxidation-reduction potential, and a negative association between acidity, organic carbon, and metals.

The content of all metals in the samples is at the background level. The only exceptions are some points of sampling where the contents of Pb, Zn, Cu, Fe, and Mn a little bit exceed the background level. Gauges III, VI, and VII showed maximum values of zinc and lead concentrations exceeding natural values in bottom sediments (by 1.2–1.9 times for zinc and 1.4–1.7 times for lead); the lower watercourse of the Belaya River revealed maximum values of copper concentration exceeding natural values by 1.2–2.0 times, and gauge VI – maximum values of iron (by 1.3 times) and manganese (by 1.6 times) concentration.

Analysis of the content of heavy metals in various layers of bottom sediments shows that it changes under the influence of a complex of endogenous factors (microterrain, activity of microbiological processes, content of organic matter, pH, oxidation-reduction conditions) and exogenous factors, including anthropogenic ones. Upper layers are more enriched with heavy metals, which is caused by their entry from the water column with biological components and flow-through binding with organic matter.

All studied sections indicate decrease in the concentrations of Pb, Zn, Cu, and Fe down the profile of bottom sediments. Insignificant content of heavy metals in bottom sediments shows quite a homogeneous vertical distribution of Zn, Cu, Pb, and Fe, which confirms an even anthropogenous loading and near optimal conditions for soil “mixing”.

Comparison of samples by bottom sediments has shown the following: in three gauge stations of seven there is a significant change in the content of Fe (gauges V–VII t=2.10–2.52), in the content of Pb – in five of seven gauge stations there is a high significance of differences in values (gauges III–VII t=3.81–12.13). High significance is also found for the content of Zn in gauges III and VII (t=5.41 and t=4.36, respectively), for the content of Cu from gauge II to gauge VII (t=2.85–16.08). This means that the samples are not homogeneous throughout the studied gauge stations.

The results have shown that valuation by Mn and Fe even the difference between the content of heavy metals in various fractions of bottom sediments within one gauge station under aerobic conditions (Fig. 2). There is no correlation between Pb concentration and main “carriers” of microelements (Fe, Mn and organic matter). High coefficients of correlation between Cu and Zn (r=0.90), Cu and Fe (r=0.63), Zn and Mn (r=0.77) indicate common sources of bottom sediments contamination with these metals.

**Figure 2.** Normalized values of Pb (a) and Mn (b) by Fe in gauge stations I–III (gauges I–II-aerobic conditions; gauge III – anaerobic conditions).

**Conclusions**

Concentration of dissolved and suspended forms of the studied elements (content of Fe, Mn, Cu, Pb, Zn, oxidation-reduction potential, pH, turbidity and water temperature) in water samples from several gauge stations of the Belaya River is characterized by heterogeneity. There is a clear tendency for the increase of the content of Fe, Mn, Zn, and Cu down the river flow with the maximum concentrations in the foothill zone of the Republic. The studied heavy metals have prevalence of the suspended form of migration.

Concentration of heavy metals in bottom sediments is considerably uneven in their distribution in different sites of the Belaya River. Practically along the entire river flow (except for the river tributaries and its mouth), bottom sediments are presented by detrital and sandy material. Bottom sediments are noticeably polluted with Zn and Pb at the village of Ministochnik, the aul of Bzhedugkhabl, and at the river mouth. In the lower watercourse of the Belaya River, contamination of bottom sediments with Cu prevails.

When oxidation-reduction zonality in bottom sediments changes, occurrence forms of heavy metals also change. The most mobile will be those heavy metals that are present most in the composition of exchange and carbonate fractions and fractions of ferromanganese oxides and hydroxides. If equilibrium conditions are violated at the contact boundary between the solid and liquid phases, especially when the pH and the oxidation-reduction conditions are reduced and in the case of the deficiency of dissolved oxygen or in the case of increased mineralization of contacting water, migration mobility of heavy metals may increase and they may transition into the aquatic environment.

In the gauge stations with low content of heavy metals, their vertical distribution is quite homogenous. In less polluted parts of the river, flowage plays an important role in vertical distribution of heavy metals. For example, with weak flowage (the part of the river from the village of Ministochnik to the aul of Bzhedugkhabl), the highest concentrations are in the surface layers of 0-10 cm in comparison to the layer of 10–30 cm. With strong flowage (Dakhovskaya stanitsa), the lowest content of heavy metals is in the upper layer of 0–10 cm, and the highest is in the layer of 10–30 cm.

The size of particles and the reduction-oxidation cycle of Fe and Mn, along with hydrological conditions and conditions of dumping of polluting substances, are the most important factors defining
distribution of heavy metals in bottom sediments of the Belaya River. The obtained high values of correlation coefficients indicate an important role of reduction-oxidation cycles of Fe and Mn, which may be crucial for the geochemical cycle of such elements as Zn and Cu.

Rating by bottom sediments reflects their granulometric variability, allows detecting sources of heavy metals entering the river system, reducing the scope of chemical and analytical work in the assessment of the existing level of heavy metals load on river ecosystems, and reducing the costs of establishing gauge stations of continuous monitoring.

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