Features Accumulation of Heavy Metals in the Bottom Sediments of Small Rivers

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Abstract. The article considers one of the aspects of anthropogenic impact on river ecosystems – the accumulation of pollutants in bottom sediments. The authors analyze the state of small rivers, the study of which is not given enough attention, while their importance for maintaining the ecological well-being of local territories and the formation of their biological diversity can hardly be overestimated. The bottom sediments of two rivers (according to V.L. Rokhmistrov's classification - the smallest and small) are being investigated for the content of heavy metal ions; the granulometric composition of sediments and the content of organic matter in them are also determined. The results of the study indicate the presence of some regularities in the distribution of certain metals in bottom sediments of the river core, heavy pollution of sediments with mobile forms of heavy metals and their possible impact on the ecological state of its own drainage basin and the state of the large river fed by them.

1. Introduction

The environmental interest of mankind, most often, is determined by the scale of the environmental problem – the more territories and population it covers, the more efforts are made to solve it. Local problems are always given less attention, whereas their existence can determine global changes in the biosphere. One of the local environmental problems is the problem of the state of small reservoirs.

In recent decades, the situation has begun to change, and small reservoirs – small rivers, lakes, reservoirs of local significance-are beginning to attract more and more attention of scientists. This is explained by the fact that their total ecological state, in fact, determines the ecological well-being of large rivers and therefore requires detailed study, protection and / or changes in the water use regime. Now, small rivers often turn out to be overloaded with various industrial and agricultural facilities, and, due to their low water content, they become accumulators of pollutants and their sources for river systems of larger orders.

Characterizing the urgency of the problem under consideration, we summarize the importance of small water bodies and list the reasons for the increase in scientific and practical interest in them:
- firstly, small rivers determine the water content and hydrological regimes of large rivers;
- secondly, they form the microclimate of the adjacent territories, regulating their temperature and air humidity;
- thirdly, these natural objects are the main factor in the formation of local ecological systems and the cause of their high biological diversity (which, in turn, determines their resistance to natural stresses and anthropogenic loads);
- fourthly, the small size of little reservoirs and their direct contact with humans explain their extreme vulnerability: the chemical composition of small rivers changes especially strongly, and then there are qualitative and quantitative changes in the components of the ecosystems formed by them;
- fifth, the change in the geochemical state of the basins of large rivers depends on the state and pollution of small water reservoirs;
- sixth, most of the small rivers remain without proper supervision: they do not have a protected zone and a greening zone, they are unkempt.

Therefore, monitoring the state of small rivers is one of the main areas of protection of both hydrological objects and the environment as a whole.

Of all the parameters characterizing the state of small water bodies, we are interested in the conditions of pollution of their bottom sediments, since the low velocities of water flow create favorable conditions for the sedimentation of various substances from their water flows to the bottom. Accordingly, the chemical analysis of bottom sediments of the objects under consideration can provide full information both on the type of anthropogenic or technogenic pollution of the river, and on its intensity.

At the initial stages of the study of small natural reservoirs, our scientific interest was drawn to two rivers belonging to the Kama River basin – the Shilna River (near the city of Naberezhnye Chelny of the Republic of Tatarstan) and the Toima River (Yelabuga district of the Republic of Tatarstan). The choice is explained by the fact that large machine-building enterprises are located on their relatively small catchment area, and most of the banks are occupied by garden societies and multiple rural settlements with private livestock farms.

2. Objects and methods
The first object of research is the Shilna River, geographically belonging to the Tukayevsky district of the Republic of Tatarstan. Its basin area is 326.4 km², the length is 49.2 km. The mouth of the river is located in the north of Naberezhnye Chelny; its lower sections are under pressure from the water of the Nizhnekamsk reservoir. The height of the river source is 190 m, the mouth is 67 m. The forest cover of the catchment area is about 15%. Shilna has a mixed power supply with a significant predominance of snow; the underground power supply module is small - 1-3 l/s·km². The average long-term annual runoff layer in the river basin is 95 mm, the flood runoff layer is 90 mm. The flood begins in late March–early April; the ice pack forms in early November. The average long-term inter-soil water consumption at the mouth of the river is 0.046 m³/s. The water is hard (6-9 mg-equiv/l) in spring and very hard (12-20 mg-equiv/l) in winter and summer. The total mineralization ranges from 300 to 700 mg/l. There is a natural monument "Borovetskii Kluchi" in the Shilna basin [1, 2]. According to the classification of V.L. Rokhmistrov the river belongs to the “smallest rivers” type [3].

The Toima River flows through several republics: its source is located in the Republic of Udmurtia, the middle current captures the Medeleevsky district of the Republic of Tatarstan, the mouth is located in the Yelabuga district of the Republic of Tatarstan. The basin area of the river is 1450 km², the length is 121 km. The large length of this river increases the height difference of its source and mouth by 29 meters. The forest cover of the catchment is slightly higher than the previous river – about 25%. The Toima also has a mixed power supply with a significant predominance of snow; the module of underground power supply is slightly larger than the Shilna River – 3-5 l/s·km². The average long-term annual runoff layer in the river basin is 146 mm, the flood runoff layer is 117 mm. The flood begins in the first decade of April, the ice is formed in the first decade of November. The average long-term inter-soil water consumption at the mouth of the river is -1.46 m³/s. The water is hard (6-9 mg-equiv/l) in spring and very hard (9-12 mg-equiv/l) in winter and summer. The total mineralization ranges from 100 to 700 mg/l. Since 1978, the Toima River has been a natural monument of the Republic of Tatarstan, and part of the Nizhnyaya Kama National Park is located in
its basin [1, 2]. According to the classification of V. L. Rokhmistrov, the river belongs to the "small rivers" type [3].

To determine the type and chemical composition of bottom sediments of the rivers under study, 4 points of soil sampling were designated on each of them:
- point No. 1 was chosen at a distance of 1 km from the source of the rivers (coordinates for the Shilna River - 55.697301, 52.490449; for the Toyma River - 56.316068, 52.409368);
- point No. 2 corresponded to the middle course of the rivers (for the Shilna River - Maloshilnenskoye rural settlement (coordinates - 55.811508, 52.531650), for the Toyma River - Pospelovskoye rural settlement (coordinates - 55.769294, 52.208181));
- point No. 3 is located 6 km upstream from the river mouths (coordinates for the Shilna River - 55.791576, 52.448505; for the Toyma River - 55.737734, 52.104841);
- point No. 4 corresponded to the mouth of the rivers (coordinates for the Shilna River - 55.737734, 52.104841; for the Toyma River - 55.741899, 52.031713).

At each point, sampling was carried out twice – in the strezhnev part of the river and in shallow water, where, due to the small flow of the river, fine particles with a possible content of pollutants are deposited at a higher speed.

The time for taking soil samples is August 2019, the second time is August 2020.

Samples of bottom sediments of the studied rivers for their analysis for pollution were taken in accordance with the general requirements of GOST 17.1.5.01-80 [4]. Determinations were carried out in each soil sample:
1) hydrogen pH index (according to the requirements of GOST 26423-85 [5]);
2) the total amount of organic matter (according to the procedure of GOST 26213-91 [6]);
3) granulometric composition (using a laser particle size analyzer);
4) concentrations of heavy metal ions (by atomic emission spectroscopy).

To analyze the pollution of river soils with ions of heavy metals, it was necessary to correlate certain concentrations of metals with their background values established in the "Regional standards "Background content of heavy metals in bottom sediments of surface water bodies of the Republic of Tatarstan" [7]. This standard provides background concentrations of various metals that may be contained in bottom sediments. These concentrations are divided into separate groups for water bodies:
- with different water flow rates (rivers, numerous types of lakes, reservoirs);
- of different origin (natural, artificial);
- with different types of bottom sediments (determined by their particle size distribution and the total amount of organic matter) (an example is given in Table 1).

| metal ions | rivers with mineral bottom sediments (organic matter content less than 30%) |
|-----------|--------------------------------------------------------------------------------|
|           | particle content less than 0.01 mm | particle content less than 0.01 mm |
|           | average value | upper limit | average value | upper limit |
| Cr        | 0.15 | 0.33 | 0.70 | 1.22 |
| Cu        | 0.53 | 1.05 | 1.16 | 1.45 |
| Ni        | 0.67 | 1.48 | 1.64 | 2.14 |
| Mn        | 85.7 | 146.8 | 301.5 | 318.3 |
| Pb        | 1.27 | 2.21 | 2.56 | 3.70 |
| Zn        | 1.37 | 3.14 | 5.93 | 7.49 |

If the actual concentration of metal in the investigated sample of bottom sediments of the corresponding type turns out to be greater than the upper limit of the background concentration, then...
for this metal the contamination factor (K_P) is calculated, which is the ratio of its actual content in the sample (C_i) and the background concentration (C_b): K_P = C_i / C_b.

The analysis of soil contamination according to the calculated pollution coefficients is carried out as follows: if K_P < 3 - moderate contamination (for this metal); if 3 ≤ K_P < 6 - significant contamination (for this metal); if the K_P ≥ 6 - the contamination is high (for this metal).

The total pollution of bottom sediments is assessed by the degree of their pollution (D_P), which is determined as the sum of the contamination factors of detected metals (K_P) for the sample under study. This estimate also depends on the amount of determined heavy metals (n) and is interpreted as follows: if D_P < 2n – bottom sediments are moderately contaminated; if 2n ≤ D_P < 4n – bottom sediments are heavily contaminated; if D_P ≥ 4n – bottom sediments are highly contaminated [4].

3. Results
At the same time with the study of bottom sediments, we conducted a study of the water quality of the small rivers under consideration, but we have not yet published the final results and their comprehensive analysis. However, we can already talk about a significant excess of the concentration of petroleum products, ammonium nitrogen, phosphates, manganese and iron ions. The previously calculated pollution indices indicate that the water quality of the studied rivers is noticeably deteriorating downstream: at points No. 1, the river waters are clean; at points No. 2, they become moderately polluted; at points No. 3 and No. 4, they are already polluted. And since the upper layers of bottom sediments are in constant contact with water masses, the indicators of their contamination should be interrelated.

Auxiliary results of the study of river soils of the studied rivers are shown in Table 2.

| sampling points | pH          | weight loss on ignition, % | content of particles smaller than 0.01 mm, % |
|-----------------|-------------|----------------------------|---------------------------------------------|
|                 | the Shilna river | the Toima river | the Shilna river | the Toima river | the Shilna river | the Toima river |
| №1  | midstream | 7.91 | 7.90 | 7.1 | 7.9 | 9.7 | 11.1 |
|      | shoal     | 7.49 | 7.78 | 6.2 | 7.3 | 16.8 | 17.4 |
| №2  | midstream | 7.52 | 8.11 | 7.5 | 8.6 | 10.8 | 13.7 |
|      | shoal     | 7.48 | 7.92 | 7.1 | 8.3 | 18.7 | 21.5 |
| №3  | midstream | 7.63 | 8.20 | 17.9 | 19.1 | 26.7 | 29.2 |
|      | shoal     | 7.57 | 7.89 | 17.4 | 18.3 | 32.7 | 35.2 |
| №4  | midstream | 7.61 | 8.33 | 28.7 | 29.5 | 18.5 | 20.7 |
|      | shoal     | 7.48 | 8.26 | 28.1 | 28.7 | 21.1 | 23.6 |

The pH indices for both rivers are slightly alkaline, which can be explained by the spread of gypsum-limestone rocks on the territory of river basins, containing underground sources feeding these rivers. In addition, the NH_4^+ ion (ammonium nitrogen) may be responsible for the increase in the pH value, the frequency of exceeding the maximum permissible concentration of which in water at some points was 10-11. At the same time, in the Shilna River, the pH decreases downstream, while in the Toyma River, on the contrary, it rises. Concerning the second river, it can be concluded that it is rather heavily polluted by runoff from large and small livestock farms located in rural settlements along the path of its flow. The Shilna River is also polluted by runoff from small livestock farms, but the natural processes of self-purification of water are still “coping” with such loads.

According to the concentration of organic matter in bottom sediments removed by them during calcination, all of them were included in the group of mineral bottom sediments with an organic content of less than 30%. However, the content of organic matter in the studied rivers noticeably increases from source to mouth, which confirms the intensity of their pollution by agricultural sources.

The granulometric composition of bottom sediments showed an increased content of silt particles for both rivers at points No. 3.
The results of the atomic emission analysis of bottom sediments for the content of mobile forms of heavy metals in them, as well as their pollution indices are given in Table 3 (the excess of the background concentration is indicated by bold).

Table 3. Content of heavy metal ions (mg/kg) in river bottom sediments.

| Metal ions | №1 | №2 | №3 | №4 |
|------------|----|----|----|----|
|            | Shilna river | Toima river | Shilna river | Toima river | Shilna river | Toima river | Shilna river | Toima river |
| midstream  | Cr  | 0.13 | 0.07 | 7.18 | 0.32 | 17.34 |
|            | Cu  | 9.08 | 1.07 | 24.40 | 0.48 | 28.46 |
|            | Ni  | 1.76 | 1.76 | 2.17 | 1.87 |
|            | Mn  | 360.34 | 792.58 | 526.15 | 1020.06 | 1182.11 | 1778.84 |
| shool      | Pb  | 294.51 | 698.37 | 327.18 | 938.67 | 861.21 | 1641.35 |
| midstream  | Kp  | 1.02 | 12.89 | 21.92 | - 27.10 |
|            | Pb  | 1.47 | 0.28 | 2.08 | 1.56 |
| midstream  | Zn  | 7.28 | 7.51 | 5.17 | 20.02 | 21.43 | 30.73 |
| shool      | Kp  | 2.45 | 5.40 | 3.58 | 6.95 | 8.05 |
| midstream  | Zn  | 5.71 | 7.76 | 8.07 | 5.18 | 20.64 | 19.15 | 32.30 |
| shool      | Kp  | 2.32 | 2.47 | 2.50 | 3.06 | 1.65 | 6.82 |

According to the conducted studies of the contamination of bottom sediments with heavy metal ions, the following conclusions can be drawn:

1) the content of chromium (Cr) and manganese (Mn) ions in the sediments of the core part of the river turned out to be higher than in shallow water areas. Thus, the distribution of the lightest ions in the sediments is not associated with an increase in their light granulometric fraction;

2) the content of copper (Cu), nickel (Ni) and lead (Pb) ions, on the contrary, was found in the core part less than in shallow water, that is, their accumulation can be associated with an increase in the number of particles less than 0.01 mm in sediments;

3) the content of zinc ions (Zn) is approximately the same, both in deep and in shallow sections of the river channel. At certain points, their concentration is higher in core sediments, at other points - higher in shallow water. These results demonstrate that there is no relationship between the granulometric composition of bottom sediments and the accumulation of zinc ions in them;

4) chromium ions appear in bottom sediments only closer to river mouths, while their content in water in different concentrations was found at all points of water sampling from No. 2 to No. 4. This behavior of chromium indicates its mobility and difficult precipitation.;

5) excess lead content was not found in any of the rivers, chromium - in the Shilna River;

6) excess of background concentrations of copper, manganese and zinc in the soils began to be observed already from the middle course of the rivers, which indicates their increased adsorption by bottom sediments;

7) the strongest pollutant was copper;

8) the accumulation of the studied metals in bottom sediments can be designated by the scheme: Pb <Ni <Zn <Mn <Cr <Cu. This series does not depend on the mass of ions and, most likely, is determined by the content of metals in river water.

Based on the excess of background concentrations for each metal (except for lead), pollution factors (KP) were determined, and then, for each sampling point, the degree of pollution (DP) of river soils with heavy metal ions was determined in total. The results showed the following:
- for the Shilna River, the pollution of bottom sediments with heavy metals is moderate along the entire course of the river (point No. 1, No. 2, No. 3) and significant at the river mouth (point No. 4);
- for the Toima river - moderate near the source (point No. 1), significant - in the middle course of the river (point No. 2) and high closer to the mouth (point No. 3) and at the mouth (point No. 4).

If we compare the results obtained with water pollution in the studied rivers, then the pollution of bottom sediments turned out to be much higher. Thus, due to the deposition and coprecipitation of pollutants, aquatic ecosystems carry out ecologically important self-purification processes for them [8]. However, heavy metals are in the bottom sediments in a mobile form, therefore, we can confidently talk about the possibility of secondary pollution of the Kama river with potentially dangerous bottom sediments, as well as floodplain meadows of the basins of the small rivers under study as a result of the removal of contaminated soil during their flooding.

4. Conclusions
We plan to expand the monitoring data of the state of small rivers by including new small rivers in the study, as well as by further monitoring the rivers under consideration. However, the already available data confirm the following:
- the accumulation of copper, nickel and lead ions in bottom sediments can be associated with an increase in the amount of fine particles in bottom sediments, therefore, these metals are deposited to a greater extent in shallow river sections;
- the deposition of such pollutants as heavy metals from water into bottom sediments occurs in small rivers quite intensively, since their waters are characterized by higher purity than soils;
- the impact of industrial enterprises and human agricultural activities on the state of small rivers is clearly traced: both the waters and bottom sediments along the river are heavily polluted, reaching a maximum at the river mouths. All this confirms the vulnerability of small rivers to anthropogenic factors;
- integral indicators of pollution of bottom sediments confirmed a high degree of their pollution with mobile forms of heavy metals, which is a potential threat to ecosystems of large rivers;
- the maximum pollution of water and bottom sediments of the studied reservoirs was found in their mouth.

5. References
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