Seasonal variability of the content of heavy metal compounds in the water of rivers in the foothills of the Central Caucasus

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Abstract. The seasonal variability of the content of heavy metal compounds in the water of the rivers of the foothill zone of the Central Caucasus (Terek, Malka, Baksan, Ardon, Cherek and Urukh) was estimated based on long-term data. Generalizing studies affecting the basin features of the level of heavy metal compounds in the river waters of the foothill zone of the Central Caucasus have not been carried out over many years. Therefore, the objective of the study was to assess the level of heavy metal compounds (Cr, Ni, Mo, Mn, Zn, Pb) in river water at six observation points located in the foothill zone of the Central Caucasus, from 2005 to 2018. An analysis of data for a 13-year period to study the level of heavy metal compounds in the Baksan, Malka, Urukh, Terek, Cherek and Ardon rivers shows that water pollution of rivers by heavy metal compounds occurs to a greater extent in the summer rain flood and has a natural character.

Introduction

When assessing water quality in river systems, the so-called priority pollutants are distinguished, which have a high toxic effect and pose a special danger to various ecosystems [1]. Heavy metals stand out among highly hazardous chemicals, because, unlike organic pollutants that decompose to some degree in natural waters, the compounds of heavy metals in them are stable and persist for a long time even after the source of pollution has been removed [2-4]. Heavy metal compounds are present in certain amounts in almost all environments, even in unpolluted (background) natural ecosystems [5-7]. Heavy metals are relatively easy to accumulate in various ecosystems, but it is difficult and very slow to get out of them, intensively accumulated by organs and tissues of living organisms. Therefore, even at relatively low concentrations, they are highly toxic to living organisms. Along with the establishment of concentrations of pollutants in water bodies, the study of the general laws of their distribution over individual sections of water bodies in different phases of the water regime is of particular importance. The works [8, 9] devoted to the study of the content and distribution of heavy metals in water bodies of the Central Caucasus are based on one-time or expeditionary studies of rivers. Generalizing studies affecting the basin-specific features of the distribution of heavy metal compounds in the river waters of the foothill zone of the Central Caucasus have not been carried out over many years. This paper presents the results of a generalization of the long-term (2005-2018) variability of the level of the content of heavy metal compounds of the highest priority for the
catchment area in the rivers of the foothill zone of the Central Caucasus in the main phases of the water regime.

Materials and research methods
Monitoring of water quality assessment is carried out annually by the laboratory of analytical chemistry of the High-Mountain Geophysical Institute by selecting river waters during routing and expedition work along the northern slope of the Central Caucasus. The rivers Terek, Urukh, Malka, Baksan, Cherek and Ardon are the objects of study.

**Terek river.** It originates on the slope of the Main Caucasian Range in the Trusovsky Gorge, from the glacier of Mount Zilga-Khokh at an altitude of 2713 m above sea level. The Terek basin belongs to the Caspian catchment area. The length of the Terek River is 623 km, the catchment area is 43,200 km$^2$. The average slope of the Terek River is 4.4 m / km. The Terek River flows into the lower Caspian Sea and the Gulf of Agrah, breaking up into a series of channels.

**Malka River.** The river originates from the glaciers of the northern slope of Elbrus and has a mountainous flow character. The Malka River is the largest left-bank tributary of the Terek; length 200 km, catchment area 10,500 km$^2$. The area of glaciation in the river basin reaches 593 km$^2$, which is about 6% of the total catchment area.

**Uruh River.** The river originates from the Digoria glaciers, the total area of which is about 130 km$^2$. In the upper reaches the river flows in a valley of a narrow gorge.

**Ardon River.** Length 102 km. It originates from glaciers on the northern slope of the Caucasian Range. The area of all 65 glaciers giving rise to Ardon is more than 70 km$^2$.

**Baksan River.** The river is 169 km long, its catchment area is 6800 km$^2$. Baksan originates from glaciers in the Elbrus region. It has many tributaries, the largest of which are the Cherek and Chegem rivers, which flow into it just above the confluence with Malka.

**Cherek River.** It is formed from the confluence of the Cherek Besengiysky and Cherek Balkarsky rivers, originating on the glaciers of the northern slope of the Main Caucasian Range and their spurs. The river is 79 km long, the catchment area is 3070 km$^2$ [10]. As mentioned above, the sources of the studied rivers are concentrated in the high mountain zone and originate from the glaciers of the Main Caucasus and Lateral ridges of the Greater Caucasus.

Water sampling was carried out at fixed points (Figure 1). When sampling water, air temperature, water and transparency were recorded. Preservation of samples was carried out with nitric acid. Under stationary conditions, the pH and the concentration of heavy metals (Cr, Ni, Mo, Pb, Zn, Mn, Cd) were measured in all samples taken. The determination of heavy metals was carried out by the atomic absorption method using an MGA-915M electrothermal atomization spectrometer [11].
The work uses long-term data on the level of heavy metals in the water of 6 rivers, at 6 observation points located in the foothill zone of the Central Caucasus, for the period from 2005 to 2018. The level of pollution of river water with hazardous heavy metals was evaluated by the frequency of exceeding the maximum permissible concentration. When assessing the pollution of surface waters, “Quality standards for water bodies of fishery value, including the standards of maximum permissible concentrations of harmful substances in the waters of water bodies of fishery value” were used. For mathematical and statistical data processing, Excel was used. “General theory of statistics” [12].

**Research results and discussion**

The long-term (2005-2018) variability of the level of water content of heavy metal compounds in rivers is shown by such characteristics as the long-term average and median concentrations, as well as by the range of concentration fluctuations (table 1). Often, the median is used as a more reliable indicator of a typical value of a trait than an arithmetic value of an average value, if a number of values are heterogeneous and include sharp deviations from the average value. The range of fluctuations is an important characteristic of the series and gives the first general idea of the difference in indicators within the population.
Table 1. Long-term average data on the levels of metal compounds (mcg/l) in the water of the studied rivers for 2005-2018 in the main phases of the water regime

| Element | Winter low water | Rain flood |
|---------|-----------------|------------|
|         | $X_{av}$ | $X_{50}$ | $X_{min}$-$X_{max}$ | $X_{av}$ | $X_{50}$ | $X_{min}$-$X_{max}$ |
| Terek River | | | | | | |
| Mo | 0.17 | 0.10 | 0.10-0.91 | 0.32 | 0.19 | 0.10-1.10 |
| Mn | 5.21 | 3.30 | 0.10-19.09 | 12.42 | 11.83 | 0.87-30.66 |
| Zn | 10.59 | 3.96 | 1.5-70.0 | 19.8 | 13.85 | 1.50-43.48 |
| Pb | 1.84 | 1.06 | 0.10-6.66 | 9.46 | 3.36 | 0.10-57.01 |
| Uruk River | | | | | | |
| Mo | 0.44 | 0.23 | 0.10-2.17 | 0.43 | 0.35 | 0.10-2.01 |
| Mn | 1.73 | 0.40 | 0.10-7.58 | 7.26 | 3.94 | 1.0-50.43 |
| Zn | 3.09 | 2.76 | 1.26-8.25 | 10.93 | 4.77 | 1.50-81.19 |
| Pb | 0.97 | 0.21 | 0.10-5.43 | 3.31 | 0.47 | 0.10-21.54 |
| Ardon River | | | | | | |
| Mo | 0.22 | 0.20 | 0.07-0.68 | 0.25 | 0.20 | 0.10-0.83 |
| Mn | 1.15 | 0.25 | 0.10-7.57 | 10.71 | 3.52 | 0.10-35.95 |
| Zn | 3.76 | 3.21 | 0.20-1.21 | 10.01 | 5.31 | 1.50-57.04 |
| Pb | 1.1 | 0.36 | 0.10-5.99 | 3.77 | 2.58 | 0.10-10.82 |
| Malka River | | | | | | |
| Mo | 0.21 | 0.10 | 0.10-1.10 | 0.30 | 0.27 | 0.10-0.64 |
| Mn | 1.28 | 0.21 | 0.10-12.01 | 7.61 | 3.69 | 0.10-47.83 |
| Zn | 3.17 | 1.50 | 1.16-14.16 | 4.35 | 2.93 | 1.50-11.21 |
| Pb | 0.63 | 0.10 | 0.10-3.32 | 1.19 | 0.33 | 0.10-4.72 |
| Baksan River | | | | | | |
| Mo | 1.27 | 0.85 | 0.17-5.06 | 2.59 | 2.14 | 0.32-8.30 |
| Mn | 1.72 | 0.31 | 0.10-14.65 | 9.15 | 3.47 | 0.10-55.90 |
| Zn | 2.29 | 1.50 | 0.88-7.49 | 6.47 | 4.43 | 1.50-22.54 |
| Pb | 1.01 | 0.18 | 0.10-8.57 | 3.31 | 0.47 | 0.10-12.66 |
| Cherek River | | | | | | |
| Mo | 0.37 | 0.10 | 0.10-2.36 | 0.39 | 0.43 | 0.10-1.04 |
| Mn | 2.32 | 0.10 | 0.10-29.67 | 6.37 | 4.34 | 1.48-22.83 |
| Zn | 2.50 | 1.75 | 1.50-6.89 | 12.70 | 6.14 | 1.50-54.57 |
| Pb | 0.69 | 0.31 | 0.10-4.17 | 4.24 | 1.14 | 0.10-15.54 |

As can be seen (table 1), the range of fluctuations in the concentration of metal compounds in the summer rain flood is higher than in the winter low-water period, with the exception of the range of Mo
fluctuations. In the water of the Malka, Urukh, and Cherek rivers, the range of fluctuations in Mo concentrations in the summer rain flood is lower than the range of fluctuations in the winter low-water season. The contents of the remaining analyzed metal compounds, such as Cr, Ni, and Cd, were significantly lower than the maximum permissible concentrations of common pollutants in water bodies for fishery purposes (MPC_{fish}), therefore, they are not presented in table 1. The repeatability of exceeding the maximum permissible concentration for heavy metal compounds over the long-term period under study is shown in Fig. 2. For Mo compounds, the highest frequency of occurrence of excess MPC_{fish} is observed in the water of the Baksan River in summer rain flood (65%).

![Figure 2. Repeatability of excess MPC_{fish} for heavy metal compounds in the water of the rivers of the foothill zone of the Central Caucasus for the period 2005-2018](image)

For Mn compounds, the highest repeatability of exceeding MPC_{fish} is observed in the water of the Terek River. In the winter low-water season it is 20%, in the summer rain flood about 60%. The highest frequency of occurrence of excess MPC_{fish} for Zn compounds is observed in summer rain flood in the water of the Terek, Ardon and Cherek rivers (52%, 45% and 40%, respectively); in the winter low-water season, the frequency of occurrence of excess MPC is much less. For Pb compounds, the
maximum frequency of occurrence of excess $MPC_{fish}$ (50%) is observed in the water of the Terek River during the summer rain flood. The proportion of samples in which during the study period there was an excess of the $MPC_{fish}$ for heavy metal compounds in the river waters of the foothill zone of the Central Caucasus did not exceed 34.5%.

**Summary**

Thus, the greatest pollution of the water of the rivers of the foothill zone of the Central Caucasus is observed during the summer rain floods, when the snow cover is melting and the debris material is washed off from the adjacent territories. The frequency of occurrence of exceeding the maximum permissible concentration of fish for the study period in the winter low-water period is 10.1%, in the summer rain flood - 24.4%.

Under natural conditions, metal ions enter surface water mainly due to weathering, leaching, dissolution of minerals and rocks that make up the catchment basin, and therefore the microelement composition of the water of the rivers under study is largely determined by the degree of interaction of water with the rock. The vertical zonality of the territory, the variety of underlying rocks and soils of the catchment areas determine the increased content of heavy metals in the water of the rivers of the Central Caucasus of glacial origin, i.e. Water pollution of rivers with compounds of heavy metals is mainly natural in nature. During anthropogenic pollution, heavy metal compounds are carried into water bodies with sewage from concentration plants, metallurgical plants, chemical industry enterprises, and mine waters. There are no such enterprises in the study area, with the exception of the Tyrnyauz Tungsten-Molybdenum Combine, which is mothballed and does not work.

As a result of monitoring and analysis of the data obtained, it is assumed that the natural factor of water pollution is mainly assumed, which leads to the excess of the $MPC_{fish}$ of the studied rivers by heavy metal compounds with the exception of the Baksan river. Adoption of basin acceptable concentrations (MPC) to improve the solution of water management problems taking into account basin features.

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