Hydrochemistry of the rivers of the Kama basin in the Northern and Middle Urals

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Abstract. The hydrochemical indicators of four rivers of the Kama basin (Kolva, Sylva, Shakva and Kishertka), flowing in the territory of the Northern and Middle Urals within the Perm region, have been analysed. It is shown that the river waters of both regions are characterized by common feeding conditions. The data of macro- and microelement analysis made it possible to carry out a modern assessment of the quality of river runoff, as well as to carry out a comparative analysis of the hydrochemical parameters of the waters of the surface runoff of two geographical regions.

1. Introduction

The territory of the Perm region has a well-developed river synodic. The rivers of the Perm Territory belong to the basin of the Kama River, the largest tributary of the Volga River, and have a mixed feeding, which is determined by climatic and geological and geomorphological conditions. During floods in the spring, the highest rises in water levels are observed, when the greatest amount of water comes from drainage basins due to snowmelt (about 60-80%). In the second place – ground water inflow, in the third – feed from precipitation. The feature of water recharge determines the amount of annual yield of drainage basin and its distribution by season [13].

Surface water, including channeled runoff, is an important element of the hydrological cycle. Due to the low salinity and lack of water resources, river waters are often used by the population for domestic water purposes. Due to the high load on them as a result of irrigation, fertilization and river disposal, surface runoff water loses its value and becomes of poor quality. Hydrochemical research allows assessing the quality and condition of water bodies. A detailed study of the hydrochemistry of surface waters in the Perm Territory was conducted by professor of the Perm State University G. A. Maksimovich. The results of his research are presented in the monograph [11]. Later, the students of G. A. Maksimovich gave a detailed description of the chemical composition and mineralization of river waters, and also compiled a hydrochemical map of the Perm region, reflecting the chemistry of river waters during the low-water period [9].

The chemical composition of rivers reflects the mineralogical features of the rocks composing the drainage basins, depends on the composition of the groundwater draining the river, and also on the inflow of pollutants into the stream canal. The data of macro-and microelement analysis of the main waterways allow to assess the quality of river flow, as well as to identify differences in the
hydrochemical parameters of the surface flow of the Northern and Middle Urals within the Perm region.

The two largest rivers of the Kama River basin (Kolva and Sylva), which have almost the same length and identical feeding conditions, were selected for research. The river valleys are composed of soluble rocks of Early Permian age, which led to the widespread development of karst here.

2. Materials and methods

The quality and condition of the surface waters of the Northern and Middle Urals waters were evaluated based on the materials obtained by the authors in the course of the work performed in 2017-2018. A total of 46 samples were collected during the study period (22 samples for chemical analysis, 24 – for trace elements) from large surface watercourses of the Northern Urals (Kolva River) and the Middle Urals (the Sylva River and its tributaries – the Shakva River and the Kishertka River). The Kolva River was tested near the village of Kamgort, which is 18 km north of the Cherdyn city. Samples from the Sylva River were collected in the Kungur city at a gauging station 100 m from the entrance to the Kungur Ice cave and in the Ust-Kishert village. In addition, the tributaries of the Sylva River – the Shakva River at the road bridge in the Plekhanovo village and the Kishertka River in the Ust-Kishert village and in the Nizkoe village were tested.

The chemical study of water was aimed at identifying organic and inorganic components, determining the degree of hardness, acidity and other indicators of suitability and quality. The selection and analysis of water samples were carried out in accordance with the requirements of quality control [3, 4]. Analytical studies of the chemical composition of water were carried out according to standard methods and GOST standards (GOST 31957-2012 p. 5.4, GOST R 56219-2014) in an accredited hydrochemical laboratory of the Perm State National Research University (accreditation certificate No.RA.RU.21HB29 dated 06.03.2018). The macrocomponent composition was determined by laboratory methods (potentiometric, photometric, titrimetric, etc.), and the microcomponent composition was determined by mass spectrometry with inductively coupled plasma on the Aurora M90 device manufactured by Bruker.

To assess the main properties and establish the chemical composition of water, a general and special analysis of water was carried out. In the process of performing a general analysis of water, according to sanitary regulations and standards (SanPiN 2.1.4.559-96), the concentration of calcium (Ca\(^{2+}\)), magnesium (Mg\(^{2+}\)), sodium (Na\(^+\)) ions, which, along with others (Cl\(^-\), HCO\(_3\), SO\(_4^{2-}\)) form the basis of six-component analysis and allow determination of iron (Fe) content and pH level. A special analysis is aimed at determining the level of hardness and acidity, the content of salts and ions CO\(_3^{2-}\), NO\(_3^-\), NO\(_2^-\), NH\(_4^+\), KMnO\(_4\) and balneological indicators in the form of trace elements such as Li, Be, Mn, Co, Ni, Cu, Zn, Rb, Sr, Zr, Mo, Cd, Pb, Sn, Cs, Ba, W, Ti, Bi.

3. Results and discussion

The Kolva River is the largest tributary of the Vishera River and the fourth longest river in the Perm region (the Kama River basin). The Kolva River basin lies in a temperate continental climate zone and is characterized by excessive moisture. The average temperature in January is \(-16 \div -18^\circ C\) (in the western and eastern parts of the basin, respectively). The average temperature in July is \(+15 \ldots +17^\circ C\) (in the northern and southern parts of the basin). From 700 to 1000 mm of precipitation falls annually. The average duration of the snow cover is 180 days, with an average height of 80 cm.

The Kolva River has an Eastern European type of water regime, with high spring flood, low summer and winter low water, and slightly increased flow in autumn. The fed of the river is mixed with a snow-fed stream. The duty of water rate varies considerably: from a minimum of 1.8\(\div\)0.8 m\(^3\)/s in March to a pronounced maximum of 860\(\div\)407 m\(^3\)/s in June; the average annual discharge rate is 165\(\div\)32 m\(^3\)/s. The freeze-up date on Kolva begins in early November and ends in late April-early May; the spring flood begins in late April [1, 14, 16, 18].

One of the largest rivers in the Middle Urals is the Sylva – the left tributary of the Chusovaya River (the Kama River basin). The river belongs to the Eastern European type with a clearly defined spring...
flood, summer-autumn rain floods and long-term stable winter low water [17]. The basin of the Sylva River is located in the zone of moderately continental climate and is characterized by excessive moisture. Annual precipitation ranges from 650 mm (southern part of the basin) to 800 mm (northern part). The duration of the snow deposits is 170-180 days. The height of the snow cover is about 80 cm. The Sylva River is a type of river with mainly snow and rain feeding, the share of underground feeding can be 15% [5]. The duty of water rate varies considerably: from a minimum of 53.1±4.0 m³/s in March to a pronounced maximum of 536.5±301.3 m³/s in May; the average annual flow rate is 1804.5±277.6 m³/s [12]. The river freezes over in November and become clear of ice in April. The largest tributaries of the river, which are also analysed in this article are Shakva and Kishertka rivers.

Table 1 shows the average hydrochemical indicators of surface channeled runoff waters obtained during the annual study period in the Northern and Middle Urals within the Perm region. The composition of the waters in the studied geographical regions is markedly different. The river waters of the Northern Urals are less mineralized (249.8±58.5 mg/dm³), have lower values of bicarbonate, sulphate ion and calcium ion compared to the waters of the Middle Urals (712.4±72.2 mg/dm³), which is directly related to the geology of the areas and the composition of the rocks composing the drainage basin. On the territory of the Northern Urals, carbonate-terogenous deposits are mainly developed, while in the Middle Urals, carbonate-sulphate deposits are developed [15]. The waters of the Kolva River have mainly HCO₃-Ca composition, but in summer and winter the Na ion appears in the composition of the waters, and in autumn and winter the Cl and SO₄ ion content increases slightly. The waters of the Sylva River and its tributaries have a constant HCO₃-SO₄-Ca and HCO₃-SO₄-Ca-Mg composition.

| Table 1. Average hydrochemical parameters of surface channel runoff waters in the Northern and Middle Urals. |
|-------------------------------------|------------------|------------------|-----------------|------------------|------------------|------------------|------------------|
|                                    | pH               | Salinity mg/dm³ | Water hardness ° | HCO₃⁻ mg/dm³ | SO₂⁴⁻ mg/dm³ | Cl⁻ mg/dm³ | NO₃⁻ mg/dm³ |
| Northern Urals                     | 7.0 ± 0.3        | 249.8 ±     | 2.1             | 132.3 ±     | 24.5 ±      | 23.9 ±      | 1.7 ± 1.0      |
| Middle Urals                       | 7.5 ± 0.8        | 712.4 ±     | ± 0.5           | 33.9 ±      | 11.1 ±      | 13.3 ±      | 3.3 ± 0.5      |
|                                    | 0.08             | 72.2        | ± 1.1           | 15.3 ±      | 44.1 ±      | 3.0         |               |
| NO₃⁻ mg/dm³                        |                  |              |                  |              |              |              |                 |
| Ca²⁺ mg/dm³                        |                  |              |                  |              |              |              |                 |
| Mg²⁺ mg/dm³                        |                  |              |                  |              |              |              |                 |
| Na⁺ mg/dm³                         |                  |              |                  |              |              |              |                 |
| K⁺ mg/dm³                          |                  |              |                  |              |              |              |                 |
| NH₄⁺ mg/dm³                        |                  |              |                  |              |              |              |                 |
| KMnO₄ mg/dm³                       |                  |              |                  |              |              |              |                 |
| Northern Urals                     | 0.4 ± 0.2        | 32.8 ±      | 6.2             | 25.2 ± 8.9  | 1.4 ± 0.7   | 0.5         | 3.7 ± 1.3      |
| Middle Urals                       | 0.2 ± 0.8        | 141.0 ±     | ± 1.7           |              | 0.9 ± 0.2   | 0.5         | 2.5 ± 0.4      |
|                                    | 0.01             | 17.7        | ± 2.3           |              | 0.2         |              |                 |

In general, as can be seen from the table, the water salinity corresponds to the maximum permissible concentration (MPC; the norm is up to 1000 mg/dm³). But if we consider individual river waters, the Kishertka River in the Middle Urals during the year has a salinity exceeding the maximum permissible concentration (1034.0-1408.0 mg/dm³). It should be noted that the chemical composition of the waters of the Kishertka River changes downstream: in the upstream water has a low mineralization (497.0-535.0 mg/dm³) due to dilution with more fresh water coming from carbonate deposits. Near the estuary of a river, the salinity increases to 1408.0 mg/dm³, this is associated with the discharge of sulphate waters in this part of the study area.

At the same time, compared with the southern region, where pH = 7.0-8.2, in the north river waters are neutral-slightly acidic (pH = 6.5-7.9) and have an increased permanganate index (3.7±1.3 mgO/dm³). This is probably due to the entry of organic substances into the river waters from the swampy areas of the Kolva River valleys and its tributaries. As known, most of the swamps in the Perm region are located in the north, north-west and west of the region [2]. It is worth noting that the
content of Cl\(^-\), Na\(^+\) and K\(^+\) in the river waters of the Northern Urals exceeds the values of the Middle Urals. Obviously, the north of the region is characterized by an intensive inflow of underground water through the fractured zones from the underlying sulphate and salt deposits of the Solikamskaya depression, which leads to an increase in sulphates, chlorides in the autumn and winter months, and sodium also in the summer.

The river waters of the northern region change their composition depending on the season and the predominant share of nourishment, while the waters of the southern region have a constant composition \[6, 7\]. In winter, when surface runoff is almost absent, the dominant role in feeding rivers belongs to the discharge of groundwater. By the content of ion, the Kolva River in winter carries a much larger set of basic ions than the groundwater tested downstream at the villages of Vilgort, Pokcha and Saltanovo. The discrepancy in the composition of the main ions indicates that a significant part of the river flow in the sampling range is formed by groundwater that feeds the river upstream. For the waters of the Sylva River, no such differences were found, the recharge is carried out by groundwater of the Irensky and Filippovsky aquifer.

Analysis and comparison of the trace element composition of river waters shows (Table 2) that in general, the content of trace elements (Li, Be, Mn, Co, Ni, Cu, Zn, Rb, Sr, Zr, Mo, Cd, Pb, Sn, Cs, Ba, W, Tl, Bi) in the Northern and Middle Urals is characterized by a low content and does not exceed the maximum permissible concentration. The exception is iron, the content of which in the waters of the surface channel runoff exceeds 2-3 times (up to 0.7-0.9 mg/dm\(^3\)). These values are recorded in the Kolva River in the summer-autumn period in the Sylva River in the Kungur city in the spring and in the Sylva River in the Ust-Kishert village autumn. The inflow of surface-slope waters rich in organic material in the spring, the inflow of water from swampy areas or the processes of waterlogging of rivers in the summer and autumn caused increased Fe values in the waters of the surface channel runoff in the Northern and Middle Urals.

Table 2. Average indicators of the trace element composition of the waters of the surface channel runoff of the Northern and Middle Urals (mg/dm\(^3\)).

| Trace element | Northern Urals | Middle Urals | MPC | Trace element | Northern Urals | Middle Urals | MPC |
|---------------|----------------|--------------|-----|---------------|----------------|--------------|-----|
| Li            | 0,004±0,001    | 0,013±0,002  | 0,03| Mo            | 0,0008±0,0001 | 0,002±0,003 | 0,25|
| Be            | 0,0005±0,0178  | 0,0005±0,008 | 0   | Cd            | 0,0005±0,0005 | 0,0005       | 0,00|
| Mn            | 0,0002±0,002   | 0,00035      | 0,10| Sn            | 0,0001±0,0001 | 0,0009       | 0,11|
| Co            | 0,0019±0,0019  | 0,0026±0,005 | 0,10| Cs            | 0,0001±0,0001 | 0,001        | 1,00|
| Ni            | 0,0042±0,0042  | 0,0017±0,0017| 1,00| W             | 0,0003±0,0003 | 0,0002±0,0008| 0,05|
| Cu            | 0,0045±0,005   | 0,0026±0,004 | 5,00| Tl            | 0,0002±0,0002 | 0,0002       | 0,00|
| Zn            | 0,0008±0,0001  | 0,0006±0,0004| 7,00| Pb            | 0,0003±0,0003 | 0,0005       | 0,03|
| Rb            | 0,13±0,09      | 0,63±0,31    | 0,07| Bi            | 0,0005±0,0005 | 0,0005       | 0,1 |
| Sr            | 0,0002±0,0002  | 0,07±0,05    | 0,1-0,9| Fe          | 0,05-0,72    | 0,3         |

Comparative analysis of trace element composition in the surface waters of the northern and southern regions of the study showed that the content of Mn, Cu, Zn, Rb, Mo, Sn prevails in river waters of the Northern Urals; Li, Co, Ni, Sr, Ba, W, Pb – Middle Urals. These differences in
concentrations are insignificant for assessing the quality of water composition, since they do not cause a threat to living organisms. The concentrations of Be, Zr, Cd, Cs, Tl, and Bi are identical for the river waters of both regions.

Single small exceedances of the MPC were detected in the waters of the Kishertka River (Middle Urals) and the Kolva River (Northern Urals): according to the content of barium (0.11-0.13 mg/dm$^3$) in summer, and lithium (0.03 mg/dm$^3$) in winter only in the southern research area in the waters of the Kishertka River.

In the spring, most trace elements are characterized by a decrease in the content due to the low mineralization of snow water.

The river waters of the studied regions have a satisfactory quality with salinity in the range of 100-1000 mg/dm$^3$, permanganate index of 0.3-6.3 mg/dm$^3$, with a total hardness of up to 9$^\circ$ and the amount of harmful impurities that does not exceed sanitary standards. The exception is the Kishertka River in the Ust-Kishert village, where the mineralization (>1000 mg/dm$^3$) and hardness (up to 19$^\circ$) exceed the MPC.

4. Conclusion
The river waters of the northern and southern regions of the study are characterized by general feeding conditions: in winter, when surface runoff is almost absent, the dominant role in the nutrition of rivers belongs to the discharge of groundwater, in spring the main source of river feeding is meltwater, and in summer and autumn – precipitation. The river waters of the Northern Urals are less mineralized. The main role in the river feeding is played by organically rich compounds – swamp waters, as well as pressure discharge of water from the underlying sulphate and salt-bearing rocks. The river waters of the Middle Urals, due to the features of the geological structure and composition of the wallrock, have increased values of mineralization, bicarbonate and sulphate ions. A certain role in the formation of the chemical composition is played by the arrival of water rich in iron during the spring flood and the swamp formation of the river. The concentrations of trace elements in both studied regions are low, mostly do not exceed the maximum permissible concentrations, and therefore, in the future, after additional studies, river water can be used for household purposes, including drinking.

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