The Role of Subaquatic Springs in the Formation of Flow, Temperature and Chemical Composition of River Water in the Reserve

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ABSTRACT

A study of the effect of subaquatic discharge of karst groundwater sources on the composition of the Vishera River, the largest tributary of the Kama River, was carried out. The study was carried out on the territory of the State Nature Reserve “Vishersky” and included the determination of the flow rate, temperature as well as chemical composition of natural waters. Six zones of karst groundwater discharge and their influence on the water regime of the Vishera river were studied in detail. It was shown that subaquatic sources in the places of their discharge, forming up to 36% of the river flow, significantly affect the temperature regime. A significant part of dissolved substances, primarily calcium ions and hydrocarbonate ions, as well as some trace elements (Li, Sr, V, Cr) enter the Vishersky river with karst waters. The results of the study show that monitoring the composition and properties of groundwater discharged covertly in the river channel is an important part of the monitoring of water bodies of both protected and developed areas.

Keywords: karst, groundwater, surface water, subaquatic springs, chemical composition of groundwater, chemical composition of surface water, river flow formation, temperature regime, nature reserves.

INTRODUCTION

Discharge of underground karst water is often in the form of underwater springs from the bottoms of rivers, lakes and seas [Maksimovich, 1961, Wirth et al., 2020; Cantú Medina et al., 2021]. It can lead to significant changes in the flow, temperature and chemical composition of river water, a decrease in dissolved oxygen and other parameters [Afgane et al., 2021; Mustafa et al., 2016; Gonneea et al., 2014]. In urban, industrial and agricultural areas, subaquatic discharge can lead to hidden pollution of rivers and lakes [Vaganov, 2017; Xilong et al, 2021; Stevanović et al., 2022]. This can significantly affect both the surface water bodies themselves and the state of the biotic components of the environment [Tamborski et al., 2020; Schubert et al., 2014]. In this regard, the study of subaquatic groundwater discharge is an important hydrogeological, hydrological and geo-environmental task [Blinov et al., 2004, Davybida et al., 2018; Pratama et al., 2021].

The mouths of subaquatic springs are under water for most or all of the year and are hidden from the eyes of observers by the water column. In this regard, the search and study of subaquatic groundwater sources is a complex task requiring the use of both conventional and special research methods [Naoura et al., 2021; Stevanović, 2019; Savatier et al., 2021]. As an example of the influence of subaquatic karst water discharge on the flow and composition of river water, this article examined the results of research conducted by Permian University staff in the territory of the Vishersky Reserve (Western Urals).

STUDY AREA

The system of state nature reserves in Russia was created in order to preserve and study the
natural course of processes and phenomena of inanimate and living nature. At the moment, there are more than 100 nature reserves in the country, which are one of the types of specially protected natural areas.

The Vishersky Reserve is located in the northeastern part of the Perm Region. The area of the protected area is 2412 square kilometers (Figure 1). There are no settlements on the territory of the reserve; the employees of the reserve live in small cordons for control functions and scientific observations.

The geological section of the reserve is represented by Riphean and Paleozoic rocks. A significant area of the Vishersky Reserve is occupied by surface outcrops of karsted carbonate rocks – limestone, dolomite, marble. The karst processes are especially active in the river valleys, which are weakened zones of fractured rocks. These zones are characterized by a large number of karst manifestations. The rivers are often absorbed by karst sinkholes and in some parts have only an underground flow, reappearing downstream in the form of powerful karst springs. Many karst springs on the territory of the Reserve are discharged subaqually, from the bottoms of rivers and karst lakes.

In this regard, the purpose of this work was to find and study subaquatic karst sources on the territory of the “Vishersky” reserve, as well as to study their influence on the flow rate, temperature and composition of river water.

METHODS

The search for subaquatic karst sources was carried out using a specially developed set of methods in several stages. The task of the initial stage was to identify the areas promising for the search of subaquatic sources. For this purpose, the analysis of topographic, geological and hydrogeological maps, as well as space and aerial photos was carried out before the beginning of expedition works. The search signs for the identification of promising areas were: the location of rivers and lakes within the limits of karst rock outcrops; borders of karst and insoluble rocks; detection of chains and fields of karst sinkholes; detection of lakes in the river sources; detection of non-freezing areas of water bodies on the winter images, etc. The data from previous studies were also analyzed [Blinov et al. 2004, 2008].

The expedition stage included prospecting works in the promising areas identified at the previous stage. Field expedition works on searching and research of subaquatic karst sources on the territory of the “Vishersky” reserve were carried out in July 2018. The section of the Vishera river from the mouth of the Niols river to a point located 2 km downstream the mouth of the Lypya river, a total length of 45 km was surveyed (Figure 2).

The survey was carried out by rafting down the river on a twin-gauged catamaran. The main search method involved thermometric and conductometric observations. The method was based
on the significant difference between the temperature and total salinity of the river water, and the groundwater of the karst springs being discharged. For this purpose, the search equipment (field instruments “Expert”) was placed on the vessel, equipped with probes for determination of water temperature, specific electric conductivity (SCE), pH indicator in situ, at a depth of up to 3 m.

Measurements were taken during rafting along the river, every 50 m. When anomalous values of temperature and SCE were detected, additional measurements were carried out with densification of the observation network, up to the visual detection of a subaquatic source. The study of the subaquatic spring included visual description and underwater photography of the spring mouth, measurement of flow and water temperature, and water sampling to determine the chemical composition.

The discharge of surface watercourses and groundwater sources was measured with a hydrometric vane. The water balance calculations
were conducted to determine the discharge of subaquatic sources, if necessary. Water sampling was carried out by a deep sampling device directly at the source mouth. Laboratory studies included total and trace element analysis of water performed in the accredited laboratories of Perm University. Cations and anions were determined by capillary electrophoresis (capillary electrophoresis system “KAPEL-105M”) as well as using the titrimetric method. The trace element composition of water was determined by inductively coupled plasma mass spectrometric analysis ICP-MS (Aurora M90, Bruker).

RESULTS AND DISCUSSION

A total of 5 large subaquatic karst springs were described during the works, which are discharged into the Vishera river channel (Spring 2V–6V). At the same time, the chemical composition, temperature and water flow were investigated in the Vishera River (Riv. V1–V3), as well as at the mouth of its large tributary, the Lopya River (Riv.L).

The Bobrovaya River is an important object of study. The flow of this river is almost entirely formed by numerous karstic groundwater sources discharging from a subhorizontal fissure in a rock outcrop of carbonate rocks (Figure 2, Photo Spring 1B). As part of the described work, a study of the Bobrovaya River at its mouth (Riv.B) was carried out, and one of the subaquatic springs that form the river flow was investigated (Spring 1B).

Table 1. Measured flow rates and temperatures of rivers and groundwater sources

| Measurement site | Distance from the initial point, km | Description | Flow rate water, L/s | Water temperature, ºC |
|------------------|------------------------------------|-------------|---------------------|-----------------------|
| Riv.V1           | 0.00                               | Vishera River, 4 km upstream of the mouth of the Lopya River | 3215                | 16                    |
| Riv.L            | 4.00                               | Lopya River, the mouth | 929                 | 16                    |
| Riv.V2           | 6.96                               | Vishera River, upstream of the mouth of the Bobrovaya River | 5425                | 13                    |
| Riv.B            | 7.75                               | Bobrovaya River, the mouth | 3114                | 6                     |
| Spring 1B        | Spring 1 (400 m upstream of the mouth of the Bobrovaya River) | 10          | 5                   |
| Spring 2V        | 11.15                              | Spring 2 (900 m upstream of the Muravy River mouth) | 829                 | 5                     |
| Spring 3V        | 11.35                              | Spring 3 (450 m upstream of the Muravy River mouth) | 298                 | 5                     |
| Spring 4V        | 11.35                              | Spring 4 (200 m upstream of the Muravy River mouth) | 188                 | 5                     |
| Riv.V3           | 15.62                              | Vishera, upstream of the mouth of the Moyva River | 16420               | 12.3                  |
| Spring 5V        | 39.34                              | Spring 5 (300 m upstream of the mouth of the Lypya River) | 434                 | 5                     |
| Spring 6V        | 40.45                              | Spring 6 (900 m downstream from the mouth of the Lypya River) | 10                  | 5                     |
| Riv.V4           | 44.61                              | Vishera River, downstream the mouth of the Lypya River | –                   | 14.2                  |

Water discharge of the Vishera River, tributaries and springs

Measurements of the river and groundwater flow rates were conducted during the summer low-water period. Atmospheric precipitation was absent during measurements from June 22nd to 25th, 2018. The measured discharges and water temperature of rivers and groundwater sources are shown in Table 1. At the initial point of the study site, which is located upstream of the surface area of karsted carbonate rocks, the flow rate of the Vishera River was 3.2 m³/s; 4 km downstream, the Lopya River flows into the Vishera River, the flow rate of which at the mouth during the period of measurements was 0.9 m³/s.

Thus, the Lopja river, which on a fairly long stretch has only groundwater flow, and the chemical composition of water which is formed, inter alia, due to dissolution of carbonate rocks, contributes almost 22% to the formation of the flow of the Vishera river. The next large tributary of the Vishera River is the Bobrovaya River, which is fed almost entirely by numerous karst groundwater sources, discharging from a subhorizontal fissure in the rock outcrop of carbonate rocks. Throughout most of the year, the fissure is located below the water level of the Bobrovaya River and the discharge occurs subaqually (Figure 3 (A)). The flow rate of the Bobrovaya River at the mouth is 3.1 m³/sec, and that of the Vyshera River before the confluence is 5.4 m³/s. The contribution of subaquatic karst sources to the total discharge of the Vishera river in this area is 36%.
Downstream of the Vishera River, several large karst springs near the mouth of the Muravy River participate in the formation of water flow (Figure 3 (B)). They are discharged subaqually into the karst lakes formed by them, the flow from which enters the Vishera River. The total discharge of these springs is 1.3 m³/s. Another large subaqueous karst spring is located at the mouth of the Sukhaya Lypya River, which in a large area has only underground flow. Here, the discharge comes from the bottom of the karst sinkhole, forming a lake, the water from which overflows into the Lypya river with a flow rate of 0.4 m³/s and further enters the Vishera river. Measurement of the water flow in the closing section (Riv.V4) under the conditions of the work was impossible due to the significant depth and velocity of the river flow.

**Water temperature of the Vishera River, tributaries and springs**

The water temperature in the Vishera River, like in other rivers, experiences seasonal and diurnal fluctuations caused by precipitation, changes in atmospheric air temperature, and other factors. The measurements of surface water temperature of the Vishera River, its tributaries and subaqueous springs were carried out during the summer low-water period, in the absence of rain with daytime temperatures of 20–25°C and nighttime temperatures of 10–15°C. In the initial point of the study site, the water temperature in the river during the day was 16°C (Table 1). The water temperature of subaqueous karst springs is stable and equal to 5°C. At the sections of the Vishera River downstream of the discharge of subaqueous springs, the water temperature decreased sharply by several degrees due to mixing with cold groundwater. At long sections downstream, there was a gradual recovery of river water temperature.

**Chemical composition of water of the Vishera river, tributaries and springs**

Hydrogen index of water of the Vishera river in the initial point of the studied area (upper streams of the Vishera river) has a neutral value (7.0–7.4). Downstream of the places of discharge of subaqueous karst sources, the pH values in the river water rise to 7.6, and at the end of the study area – to 8.0 (Figure 4). Thus, the general regularity of the growth of the river water pH index of the Vishera River was revealed. Vyshera River, caused by the inflow of karst source waters. This is due to the fact that a major role in the formation of the chemical composition of groundwater of karst massifs is played by the dissolution of carbonate rocks. As a result of dissolution of carbonate ions, the water of subaqueous springs becomes slightly alkaline, with the pH values of 7.9–8.2.

The water of the Vishera River throughout the entire study area is ultra-fresh, with salinity less than 100 mg/L (Table 2). Water composition is hydrocarbonate-calcium. There is a gradual increase in water salinity from the beginning of the studied area to its end from 20 to 60 mg/L. An increase in water salinity occurs mainly due to an increase in bicarbonate ion and calcium ion (Figure 5); to a much lesser extent, it is caused by an increase in sulfate ion, magnesium and sodium ions.

Chloride ion and potassium ion appear in tangible amounts in the water of the Vishera River only downstream of the mouth of the Lypya River (Riv.V4). It should be noted that the permanent residence of the reserve’s employees is located...
in the mouth of the Lypya River. There are no places of permanent residence upstream of this section along the river.

The salinity of water of subaquatic karst sources is higher than the salinity of river water and is 100–128 mg/L (Table 2). The composition of water is calcium-hydrocarbonate, with \( \text{HCO}_3^- \) and \( \text{Ca}^{2+} \) accounting for more than 90% of the total mineralization. Sulfates, nitrates, magnesium and sodium ions are present in small amounts. Chloride ions and potassium were not detected by chemical analysis.

### Trace element composition of water of the Vishera River, tributaries and springs

The study of the trace element composition of groundwater and surface water (Table 3) allowed distinguishing three groups of elements.

The first group includes the elements the content of which in the groundwater of karst sources is significantly higher than in the water of the Vishera River. Such elements include alkaline earth metals Li and Sr, which along with Ca and Mg are present in increased concentrations in carbonate rocks [Sklyarov, 2001]. An expressive example of elements from this group is strontium. In the water of subaquatic karst springs the strontium content is 1.5–2 times higher than in the water of the Vishera river. As a result, of the fact that the feeding of the river is largely due to subaquatic karst water discharge, the concentration of elements of this group in the river water increases downstream (Figure 6). The metals V and Cr also belong to this group.

The second group includes elements the content of which in groundwater is much lower than in the river water. These elements include Y, Zr and Ce (Table 3, Figure 7). The concentration of these elements in the river water decreases downstream of the Vishera river due to a significant inflow of subaquatic spring waters.

The third group includes the elements the content of which in groundwater and surface water is approximately the same or changes in concentration do not have clear relationships.
| Sampling point | pH | HCO$_3^-$ | SO$_4^{2-}$ | Cl$^-$ | NO$_3^-$ | NO$_2^-$ | Ca$^{2+}$ | Mg$^{2+}$ | Na$^+$ | K$^+$ | Mineralization |
|----------------|----|-----------|-------------|-------|---------|---------|---------|---------|-------|-------|----------------|
| Riv.V1         | 7.4| 15.0      | 1.41       | b/d   | b/d     | b/d     | 3.9     | 0.76    | 0.99  | b/d   | 22.0           |
| Riv.V2         | 7.0| 33.8      | 1.52       | b/d   | b/d     | b/d     | 8.4     | 1.06    | 0.70  | b/d   | 45.5           |
| Riv.B          | 8.1| 74.1      | 2.0        | b/d   | 0.59    | b/d     | 20.4    | 1.78    | 0.8   | b/d   | 99.6           |
| Spring 1B      | 8.2| 72.8      | 2.1        | b/d   | 0.49    | b/d     | 21.1    | 2.12    | 0.9   | b/d   | 99.4           |
| Spring 2V      | 8.0| 78.2      | 2.2        | b/d   | 0.59    | b/d     | 23.1    | 1.99    | 0.9   | b/d   | 106.9          |
| Spring 3V      | 8.0| 75.4      | 2.2        | b/d   | 0.60    | b/d     | 23.5    | 2.21    | 0.9   | b/d   | 104.7          |
| Spring 4V      | 8.1| 76.9      | 2.2        | b/d   | 0.58    | b/d     | 22.8    | 2.12    | 0.7   | b/d   | 105.3          |
| Riv.V3         | 7.6| 45.8      | 1.7        | b/d   | 0.17    | b/d     | 12.8    | 1.26    | 0.66  | b/d   | 62.4           |
| Spring 5V      | 7.9| 91.7      | 5.4        | b/d   | 0.50    | b/d     | 25.8    | 3.65    | 0.7   | b/d   | 127.7          |
| Spring 6V      | 7.9| 88.6      | 3.4        | b/d   | 0.23    | b/d     | 27.0    | 2.36    | 0.7   | b/d   | 122.3          |
| Riv.V4         | 8.0| 42.8      | 2.03       | 3.2    | 0.28    | b/d     | 12.9    | 1.43    | 1.99  | 2.3   | 67.0           |

**Note:** 1) sampling points in the Vishera River are highlighted in bold; 2) b/d: below the detection limit; 3) sampling points in the table are arranged in the order of the route down the Vishera River.

| Element | Riv.V1 | Riv.V2 | Riv.B | Spring 1B | Spring 2V | Spring 3V | Spring 4V | Riv.V3 | Spring 5V | Spring 6V | Riv.V4 |
|---------|--------|--------|-------|-----------|-----------|-----------|-----------|--------|-----------|-----------|--------|
| Li      | 0.04   | 0.08   | 0.13  | 0.12      | 0.10      | 0.09      | 0.07      | 0.12   | 0.95      | 0.49      | 0.12   |
| Sr      | 12.8   | 18.2   | 24.6  | 26.1      | 30.7      | 32.4      | 30.3      | 21.6   | 42.7      | 38.5      | 21.9   |
| V       | 0.81   | 1.14   | 1.69  | 1.37      | 1.45      | 1.82      | 1.58      | 1.11   | 1.82      | 1.71      | 1.36   |
| Cr      | 2.4    | 3.6    | 5.6   | 4.6       | 4.9       | 6.2       | 5.2       | 3.5    | 6.1       | 5.8       | 4.4    |
| Li      | 0.31   | 0.19   | 0.05  | 0.05      | 0.03      | 0.04      | 0.03      | 0.03   | 0.18      | 0.13      | 0.18   |
| Mn      | 0.40   | 0.67   | 0.13  | 0.05      | 0.02      | 0.02      | 0.03      | 0.90   | 0.12      | 0.07      | 0.56   |
| Cu      | 1.36   | 0.01   | 0.05  | 0.15      | 0.16      | 0.01      | 0.18      | 0.01   | 0.06      | 0.01      | 0.08   |
| Y       | 0.12   | 0.07   | 0.02  | 0.02      | 0.02      | 0.02      | 0.01      | 0.06   | 0.03      | 0.05      | 0.04   |
| Zr      | 0.08   | 0.05   | 0.02  | 0.02      | 0.02      | 0.02      | 0.01      | 0.05   | 0.04      | 0.05      | 0.04   |
| Ce      | 0.10   | 0.08   | 0.03  | 0.03      | 0.03      | 0.03      | 0.06      | 0.04   | 0.05      | 0.04      | 0.05   |
| Co      | 0.03   | 0.02   | 0.02  | 0.03      | 0.03      | 0.03      | 0.03      | 0.02   | 0.02      | 0.01      | 0.02   |
| Ni      | 0.21   | 0.05   | 0.06  | 0.04      | 0.07      | 0.08      | 0.06      | 0.11   | 0.18      | 0.22      | 0.08   |
| Zn      | 1.2    | 1.6    | 1.7   | 1.8       | 1.7       | 1.5       | 1.7       | 1.6    | 1.6       | 1.6       | 1.7    |
| Ga      | 0.03   | 0.04   | 0.05  | 0.03      | 0.04      | 0.05      | 0.04      | 0.03   | 0.04      | 0.03      | 0.04   |
| Ge      | 0.2    | 0.17   | 0.13  | 0.21      | 0.18      | 0.15      | 0.16      | 0.19   | 0.22      | 0.21      | 0.16   |
| As      | 0.08   | 0.06   | 0.14  | 0.04      | 0.15      | 0.1       | 0.15      | 0.16   | 0.08      | 0.05      | 0.04   |
| Se      | 1.5    | 1.2    | 2.5   | 3.8       | 3.3       | 3.5       | 2.1       | 0.8    | 0.4       | 1.8        | 1.8    |
| Rb      | 0.14   | 0.08   | 0.1   | 0.07      | 0.1       | 0.17      | 0.09      | 0.12   | 0.28      | 0.2        | 0.14   |
| Be      | 0.002  | 0.002  | 0.01  | 0.008     | 0.016     | 0.004     | 0.014     | 0.008  | 0.004     | 0.004      | 0.010  |
| Mo      | 0.07   | 0.11   | 0.65  | 0.1       | 0.19      | 0.39      | 0.13      | 0.08   | 0.23      | 0.11       | 0.13   |
| Ba      | 12.2   | 11.9   | 12.6  | 12.2      | 14        | 12.5      | 13.7      | 11.9   | 14.2      | 11.8       | 10.7   |
| Pb      | 0.1    | 0.13   | 0.13  | 0.14      | 0.14      | 0.13      | 0.13      | 0.13   | 0.13      | 0.13         | 0.14  |

**Note:** 1) sampling points in the Vishera River are highlighted in bold; 2) sampling points in the table are arranged in the order of the route down the Vishera River.
Figure 7. Concentrations of zirconium and cerium in waters of the Vishera River and waters of karst springs

CONCLUSIONS

The study of the properties and composition of ground and surface waters in the 46-km section in the upper streams of the Vishera river has shown that the powerful discharge of subaquatic karst springs plays a significant role in the formation of the river flow. The contribution of the largest springs to the formation of the river flow is 22–36% of the total flow of the Vishera river.

A significant component of the underground feeding of the river leads to a decrease in the temperature of the river water by several degrees in the areas located downstream from the springs.

Due to the powerful subaquatic discharge of karst waters, significant changes in the chemical composition of the Vishera river water are observed. The hydrogen content increases from neutral values in the upper part of the section downstream to slightly alkaline values. Mineralization
increases from 22 to 67 mg/l primarily due to increased content of hydrocarbonate ions and calcium ions. Downstream in the investigated section, the concentrations of alkaline earth metals as well as V and Cr increase in the river water. In contrast, the concentrations of Al, Ti, Mn, Cu, Y, Zr, and Ce decrease.

Such changes in the chemical composition are associated both with the features of the chemical composition of karst carbonate rocks, due to the dissolution of which the composition of groundwater is formed, and with the conditions of migration of chemical elements in the studied area of the Vishera river. The results obtained significantly complement and extend the knowledge of hydrogeological, hydrological and hydrogeochemical features of the territory of the “Vishersky” reserve. At the same time, the results of the study show that monitoring the composition and properties of groundwater discharged covertly in the river channel constitute an important part of the monitoring of water bodies of both protected and developed areas.

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