HYDROCHEMICAL CHARACTERISTICS OF THE LARGE KARST SPRINGS IN THE CATCHMENT OF MESTA RIVER (BULGARIA)

Boyka Mihaylova, Konstantin Kostov, Aleksey Benderev

Received on March 16, 2022
Presented by I. Zagorchev, Member of BAS, on June 21, 2022

Abstract

Mesta river is a cross-border river with Greece, whose catchment area includes parts of Rila, Pirin and the Rhodope Mountains. The karst is developed in pre-Paleozoic marble that forms isolated outcrops with different basins. The largest of them forms two alpine karst basins located in Northern Pirin and Slavyanka Mountains. In the Rhodopes region, the marble outcrops are fragmented and embedded in non-karstic rocks. They are drained from springs with relatively low flow rates. The largest karst springs drain different hydrodynamic zones of the karst massif of Northern Pirin. From the karst basin of Slavyanka Mountain, only the large subthermal spring near the village of Musomishta falls into the catchment area of the Mesta river. The data on the chemical composition of some of the karst springs are summarized, paying attention to the largest of them. An analysis of the changes in the chemical composition and comparison is made. The changes of the hydrochemical parameters of the springs draining different vertical zones in Northern Pirin are compared. The obtained results prove that the main role in the formation of the chemical composition of karst waters has natural factors – interaction between water and marbles. It was found that the waters are unsaturated to carbonate minerals, which proves that even now there are active processes of karst formation.

Key words: Mesta river basin, karst springs, chemical composition

This work has been carried out in the framework of the National Science Programme “Environmental Protection and Reduction of Risks of Adverse Events and Natural Disasters”, approved by the Resolution of the Council of Ministers No. 577/17.08.2018 and supported by the Ministry of Education and Science (MES) of Bulgaria (Agreement No. DO-230/06-12-2018).

DOI:10.7546/CRABS.2022.11.08
Introduction. Along with cross-border rivers between Bulgaria and Greece Struma/Strymon and Maritsa/Evros, the Mesta/Nestos is one of the three main fluviolacustrine systems in the Northern Peri-Aegean Region that were set on in Middle Miocene and lately developed in Late Miocene, Pliocene and Quaternary time \[1\]. Therefore, it is important to know well the conditions and factors influencing the quality of its waters. One of the sources forming part of the river’s outflow is groundwater. The karst areas are spread over significant part of the Mesta river’s catchment area in both countries. The aim of the present study is to establish the main features and regularities of the chemical composition of the larger karst springs, which are an important part of the river outflow.

Characteristics of the catchment area. The Mesta river catchment area is located in southeastern Bulgaria (Fig. 1) and has an area of 2767.1 km\(^2\) \[2\]. The catchment area includes parts of some of the largest mountains of Balkan Peninsula – Rila, Pirin and the Rhodopes. Its average altitude is 1310 m, which is the reason for the high water abundance – runoff modulus of 15 l/s/km\(^2\). The total length of the river is 273 km with 126 km on Bulgarian territory where it receives about 25 tributaries. Mesta river leaves the country and enters the territory of Greece south of the village of Godeshevo. The river named Nestos flows into the Aegean Sea east of the resort village of Keramoti. The average outflow of the river when leaving Bulgaria is about 30 m\(^3\)/s, varying in a wide range according to the season.

Most of the catchments are characterized by the mountainous nature of the relief. The only flat areas are the imposed Razlog and Gotse Delchev valleys, the formation of which is due to tectonic reasons – they are developed along tectonic grabens \[3,4\]. Pre-Cambrian metamorphites, granitoides of different age, Paleogene sediments and effusives are found in the catchment area. The graben-shaped hollows are filled by Neogene and Quaternary sediments. From hydrogeological point of view the fissured waters in the granites and metamorphites, the karst in the marbles and the pore waters in the sediments of the valleys are predominant. A number of thermal water deposits are attached to faults.

In regional terms, the chemical composition of surface waters has been characterized by Yordanov \[2\], and more recent studies and summaries have been performed by Yotova et al. \[5\], and on groundwater by Vasileva and Toteva \[6\], Vasileva \[7\], and Vasileva and Sholev \[8\].

Karst and karst waters. In the catchment of Mesta river, the rocks of the Dobrostan Formation were subjected to karstification \[9\]. The formation is up to 1000 m thick and consists of massive or striped medium-grained marbles, in places with layers of gneiss. In the western part of the catchment area of the Mesta river the marbles form two larger outcrops (Fig. 1), form independent karst basins – in Northern Pirin and in Southern Pirin and Slavyanka \[10-12\]. In the Rhodopes, the marble outcrops are fragmented due to tectonic causes and form several small
Northern Pirin is a typical alpine karst basin \cite{13}, which is entirely disposed in the catchment of the Mesta river. Within the range of the karst basin two of the highest peaks of the Balkan Peninsula are located – Vihren (2914 m) and Kutelo (2908). The drainage zones are at an elevation of 920–940 m. As a result, the snow feeding and the high aggressiveness of these waters play an important role in the formation of karst. With a total area of marble excavation of about 45 km$^2$, about 170 caves have been established here, and the runoff is about 20 l/s.km$^2$ \cite{12,13}. Potholes are predominant, including the second deepest cave in Bulgaria – the system “Banski Suhodol 9-11” with a depth of over 400 m and a total length of 1158 m. Some of the surface karst forms and the entrances of the potholes have long-term ice accumulations. The high degree of karstification of the extremely thick aeration zone, the mountain climate with high precipitation and thick snow cover are the reason for the presence of springs with very high flow rates. They are characterized by dynamic regime and drainage of maximum water quantities.
in early summer, when the most intensive snowmelt processes begin. The main springs that drain the karst basin are located at the base of the mountain (Fig. 1) – Yazo and Kyoshka. They form the outflow of Iztoka river – right tributary of the Mesta river. Their total water quantities vary in the range of 400 to more than 5000 l/s. There are other sources, but they have a lower flow rate. With relatively higher flow-rate – from 50 to over 200 l/s is the spring "Kalugeritsa" located in the northernmost part of the basin, at a relatively higher elevation – 1470 m.

The karstified marble has the greatest distribution in South Pirin and Slavyanka Mtn (Fig. 1) – a total of over 300 km² and forms a large karst basin with transborder and trans-river basin character [14]. Less than a quarter of this basin (72 km²) disposed into the catchment of the Mesta river in Bulgaria. The other marble outcrops are located on the territory of Greece and the catchment of Struma river. A granite intrusion is embedded in the marble body, through which the watershed between Mesta and Struma passes. The karst in this basin also has a mountainous character. Due to the relatively lower altitude (the highest peak of Gotsev Vrah is 2212 m) and with increased Mediterranean climatic influence, the role of snow cover on the amount and regime of karst waters is lower than in Northern Pirin. Another significant difference is that unlike Northern Pirin, where the karst landscape is typically naked, alpine, in this basin, the karst is partly covered. On Bulgarian territory, 50 caves and potholes have been registered, half of which are located in the catchment area of the Mesta river. The caves are not large – the longest is 145 m and the deepest 86 m. The larger caves are on the territory of Greece, where the main drainage zone of the karst basin with the largest karst springs is located. Two drainage zones have been established on the territory of Bulgaria. One is located in the catchment area of Struma river, with a main spring near the village of Petrovo. There are two large springs in the catchment area of Mesta river and they drain karst zones in South Pirin. The Breznitsa spring with a flow rate of 100–160 l/s drains the northernmost, relatively higher parts of the basin. At the eastern foot of South Pirin a group of subthermal springs are located near the village of Musomishta, with total water flow rate often above 2000 l/s and temperature 20–25 °C. The location of the group of springs is determined by the tectonic contact of the marble with deposits filling the Mesta graben. The inflow of warmer karst waters from depth is connected with the fault structures. In the eastern part of the catchment, within the Rhodopes, a number of small marble outcrops with an area of several hundred square meters up to about 20 km² and a total area up to 35 km² are established. As a result, the degree of karstification is lower. Only 17 small mainly horizontal caves have been explored. As an exception, in one of these marble bodies with an area of less than 1 km², the longest cave in the catchment area of Mesta river is located – Manoilova Cave (2176 m and depth of 116 m) near the village of Ribnovo. The cave is formed
by surface waters, which, when entering the marble outcrop, pass this section under the ground and come to the surface again when leaving it. In most of the outcrops the fissure waters and, to a lesser extent, fissure-karst waters are predominant. Some springs in the largest outcrop in this part of the catchment (Satovcha basin) – the springs Sedemte Chuchura and Ablanitsa, as well as two subthermal karst springs in the valley of Mesta near the villages Slashten and Godeshevo have relatively high flow rate – up to several liters.

**Results and discussion.** To characterize the chemical composition, the main karst springs in the catchment area of the Mesta river were visited (Fig. 1). The results of analyses of their waters in the past were also collected and systematized. The characterization of the chemical composition of springs in Pirin is performed on the basis of summarizing a different number of analyses – from 17 for the spring Breznitsa to over 50 for the spring Yazo. The sampling period is from the 60’s until now. Most of the samples were taken between 1960 and 1980, and after 2000 the number of samples decreased sharply, but no significant differences were observed in the two periods. For the springs located in the Rhodope Mountains, only the samples taken during the present study were used.

It was found that the karst waters in the catchment area of the Mesta river have a low TDS (Fig. 2) and a pH from 6 to 8.86, most often between 7 and 7.5. By type, hydrogen carbonate-calcium waters predominate, but in some of the springs an increased sodium content is also found (Fig. 3). The low mineralization and the high degree of karstification are the reasons why the waters have a significant potential for dissolving the carbonate rocks – the saturation index (SI) of calcite is everywhere below 0. The TDS of the Kyoshka spring changes in the widest range, but this may be due to the fact that almost twice as many water samples were taken from it in different climatic conditions, and for a longer period of time than for all other sources. With relatively low average TDS are the springs located at the highest altitude and with a relatively shorter path of water movement – Kalugeritsa and Breznitsa. The Breznitsa spring is characterized by a relatively high solubility in terms of calcite, due to the significant role in their recharge by incoming alpine waters from granite outcrops. The subthermal complex of springs near the village of Musomishta has the highest values of TDS. Only the waters from these springs in the considered area are periodically saturated with regard to calcite, which is confirmed by travertine deposits around them. The fissure and fissure-karst springs in the Western Rhodopes are with higher values of TDS – from 440 to 530 mg/l. The saturation index is also below 0 – from −0.07 to −0.22.

The main role in forming the chemical composition of the waters have the host rocks – marbles. With the increase of TDS, the contents of hydrogen carbonates, calcium and magnesium ions also increase (Fig. 4). It was found that this relationship is much clearer for the hydrogen carbonates. This is due to the unequal presence of sodium in the recharging waters coming from areas with pres-
ence of granites and gneisses. This is best expressed for the high located springs Kalugeritsa and especially Breznitsa, where in the catchment area of the spring there are embedded granite bodies (Fig. 3).

To clarify the conditions of drainage of the karst basin in Northern Pirin, an analysis and comparison of the chemical compositions of the two major springs –
Yazo and Kyoshka, that drain it and are located close to each other, was made. It was found that their chemical composition is relatively similar, but no coincidence of changes in time was observed. No correlation was found between any of their hydrochemical characteristics, although the values of most of them are too close. This indicates that although the karst waters have a general nature, other factors are important for the final formation of their chemical composition.

Regarding the microcomponents in some springs, quite low concentrations of some heavy elements, arsenic, chromium and other elements related to the host rocks are rarely found, but they do not affect the excellent ecological condition of the karst waters. H$_2$SiO$_3$ is found in the subthermal springs – in the order of 20 mg/l, and sometimes barium and lithium.

**Conclusion.** The areas of distribution and formation of karst groundwater occupy a relatively small area – about 5% of the catchment area of the Mesta river, but they are characterized by relatively higher water abundance than most widespread silicate rocks. Therefore, they are essential for the formation of the chemical composition of surface waters. The analysis of the hydrochemical features of the karst groundwater shows that they are clean and are a factor for improving the ecological condition of surface waters in the catchment area of the Mesta river. This is largely due to the insignificant anthropogenic impact in their catchments. Unlike the groundwater in the rest of the catchment, the water here is mainly HCO$_3$-Ca-Mg. Elevated contents of sodium and sulphates are found in springs, in the surface catchment of which there are outcrops of granites and gneisses. Another hydrochemical feature of karst waters compared to waters in fractured silicate rocks is the relatively wider range of TDS variation due to the change in contact time between groundwater and carbonate rock at low and high flow rates of the large karst springs. It was found that regardless of the change of the hydrodynamic situation during the dry and wet periods the values of the saturation index are negative, which proves that the processes of dissolution of carbonate substance and active karst processes in the marble massifs predominate.
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Geological Institute
Bulgarian Academy of Sciences
Akad. G. Bonchev St, Bl. 24
1113 Sofia, Bulgaria
e-mail: boyka_m@abv.bg
kskostov@geology.bas.bg
alekseybenderev@yahoo.com

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B. Mihaylova, K. Kostov, A. Benderev