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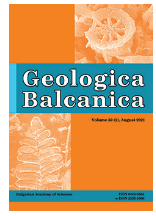

Groundwater chemistry: a case study of the Mesta River Basin

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Abstract. The present study describes the hydrochemistry of ground waters found in the Mesta River Basin, located in the south-western part of Bulgaria. The groundwater's composition can be expressed as follows: $Ca^{2+} > Na^{+} > Mg^{2+} > K^{+}$; $Ca^{2+} > Mg^{2+} > Na^{+} > K^{+}$ in equivalent units for the cations, and $HCO_3^{-} > SO_4^{2-} > Cl^{-}$ in equivalent units for the anions. The chemical composition of the studied groundwater can be described as calcium-bicarbonate. The calcium ions make up from 17.90% to 38.62% (30.18% on average), and the bicarbonate ions make up from 35.30% to 48.98% (43.70% on average) of all ions. Taken together, the calcium and bicarbonate ions make up from 61.44% to 87.60% (73.88% on average) of all ions. The groundwater itself is of slightly alkaline nature, having pH of 7.3 to 8.6, and TDS of 67 mg/l to 611 mg/l. One groundwater sample from the Mesta River catchment area was found to be of the low-mineralized type (TDS = 193 mg/l) alkaline water (pH = 9.8) in the Mesta Lowlands – the Banichan groundwater mineral source. The water can be described as sodium-bicarbonate, with sodium ions making up to 93.5% of the cations, and bicarbonate ions – 69.6% of the anions. Out of all ions, the sodium ions were found to be 48%, and the bicarbonate ions – 33.86%. The sequence of ions is in the following order: $Na^{+} > Ca^{2+} > Mg^{2+} > K^{+}$, and $HCO_3^{-} > Cl^{-} > SO_4^{2-} > CO_3^{2-}$.

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INTRODUCTION

The factors determining the geological setting for groundwater formation and its composition can be quite diverse. Their intensity can be related to any particular natural environment. The groundwater's composition, dynamics, and regime are affected to a large degree by physical-geographical factors, such as relief, climate, hydrology, and also by geological factors, such as the geological make-up and lithological composition of the rocks. The present study analyzes the natural chemical composition of groundwater samples from the Mesta River catchment area (taken in the month of September, 2020). Twelve natural exits of groundwater (in the form of springs) were analyzed. Some of those springs were tapped. Another aspect of the study is presenting data from the chemical analysis of a water sample taken from an abandoned well, located at the Banichan mineral water deposit. This study undertakes the task of establishing the hydrochemical facies of groundwater found in various genetic rock types.

Up until now, much research has been done regarding the chemical quality of groundwater in the Mesta River Basin. The results of several monitoring observations, as well as other hydro-chemical

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studies, focused mainly on the ecological status of groundwater, have been summarized in the River Basin Management Plan for the West Aegean region. The data can be found on the website of the Executive Environment Agency (http://www.eea.government.bg/), as well as on the web page of the Basin Directorate responsible for the West Aegean region (https://wabd.bg/content/). At present, the Basin Directorate of the West Aegean region performs monitoring activities related to the quality of groundwater at 21 monitoring points (18 controlling points and three points for operative monitoring) of the Mesta River Basin. The purpose behind this monitoring process is to evaluate the quality of groundwater found in individual administrative units – the so-called groundwater bodies (GWBs). This monitoring is of prime importance for maintaining the ecological status of groundwater in the respective GWBs, and serves as a vehicle for establishing territorial differences in groundwater sources and various anthropogenic pressures on the quality of groundwater. The aim of the present study is to collect not only samples from the same sources as the monitoring points in the West Aegean region, but also to collect the necessary data for hydro-chemical analysis of groundwater found in different types of rocks.

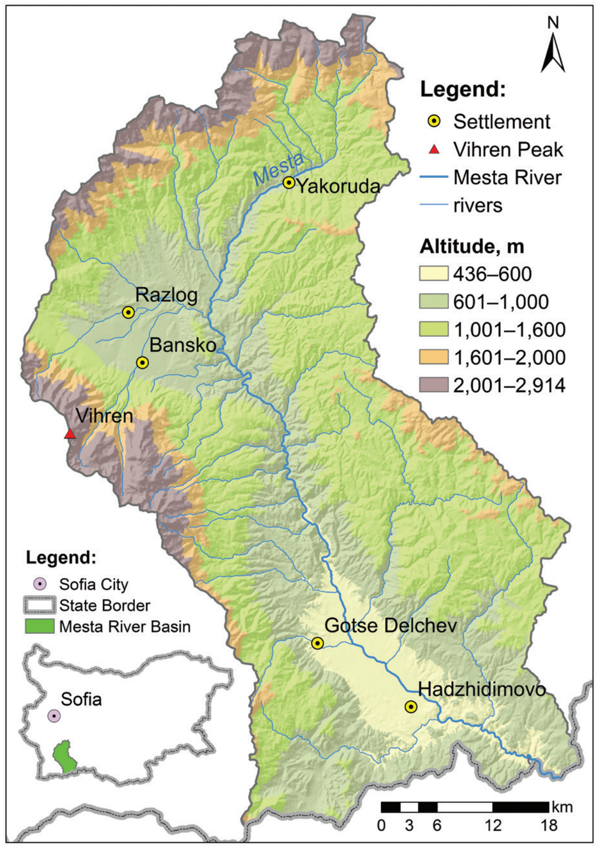

Fig. 1. Location of the Mesta River Basin.

LOCATION, GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

The studied area is located in the south-western part of Bulgaria (Fig. 1), and has an area of 2,785 km^2. It includes the Mesta River Valley (along with its tributaries), parts of the Rila and Pirin Mountains, as well as the western Rhodopes. The Razlog and Gotse Delchev Lowlands are also located in this region. According to data obtained from digital elevation models (http://srtm.csi.cgiar.org/), the topography of the catchment area can be described as consisting of low mountains with an altitude of 600–1,000 m (30.3%), and mountains of average height (1,000–1,600 m; 44.3%). These are complemented with denudation plains, quite dissected in certain areas.

Hilly relief (200–600 m) covers 7.5% of the Mesta River Basin, and the high-mountain relief, with an altitude above 1,600 m, is about 18%. The average altitude of the catchment is about 1,224 m. The annual precipitation for the period 1931–1985 for the Bansko Station was recorded as 694 mm, and for the Gotse Delchev Station – 695 mm (Koleva and Peneva, 1990). The average annual air temperature for the period 1931–1970 was 9 °C for the Bansko Station, 11.4 °C for the Gotse Delchev Station, and 3.5 °C for Vihren Hut (Kyuchukova, 1983). As a whole, the soil cover consists mainly of cinnamon and brown forest soils (Georgiev, 1991). According to CORINE Land Cover data (CLC, 2006 – https://land.copernicus.eu/pan-european/corine-land-cover/clc-2006), about a half of the catchment area (nearly 54%) is occupied by forests. Coniferous, rather than deciduous, vegetation predominates in the studied region.

The geological background is relatively complex, with interesting relationships between magmatic, metamorphic, sedimentary, and volcano-sedimentary rocks. According to the most recent geological map sheets in scale 1:50 000, both Precambrian metamorphites and Paleogene plutonic rocks have the widest prevalence (Milovanov *et al*., 2009a, b; Klimov *et al*., 2010a, b; Sarov *et al*., 2009a–c, 2010a–d, 2011a–c). Those rocks form the geological setting for the existing porous, cracked, and karst waters. The former are accumulated in the Pliocene and Quaternary deposits, distributed in the youngest graben structures (Razlog and Gotse Delchev valleys). Crack-waters form the aquifer system in the regional cracking zone in the mountainous and low-mountainous zones of Rila and Pirin, as well as the westernmost parts of Western Rhodopes. These are the most widespread types of groundwater that can be found in the studied region, and are used for drinking purposes, coming from captive springs, by many settlements.

DATA ACQUISITION AND METHOD OF STUDY

The baseline for this study is data of the chemical composition of groundwater samples taken from localities in the Mesta River Basin. The geographical coordinates of each hydrogeological element were taken into account. Each element was fixed with its latitudinal and longitudinal coordinates expressed in decimal degrees. Topographic characteristics were measured in terms of altitude expressed in meters. Temperature and hydrogen-ion activity (pH) of groundwater were measured in the field. The groundwater samples and their chemical composition were analyzed at Aquaterratest Laboratory. They were taken in September, 2020. Of all 13 samples, 12 were obtained from springs and one came from a borehole. As a whole, 17 physical and chemical constituents of groundwater were taken into account. The major, and commonly analyzed, elements were the following: total dissolved solids (TDS), total hardness (TH), electrical conductance (EC), permanganate oxidizability (PO), F^-, Cl^-, NO_2^-, NO_3^-, PO_4^{3-}, SO_4^{2-}, HCO_3^-, CO_3^{2-}, NH_4^+, Ca^{2+}, K^+, Mg^{2+}, and Na^+. The TDS and TH were determined by means of calculations. The temperature and pH were measured on location, and allowed to stabilize before the collection of samples, while their chemical parameters were determined analytically. The hydro-chemical facies of groundwater are given according to the Piper Diagram (Piper, 1944) and Chadha Diagram (Chadha, 1999), which represent a graphical procedure for interpreting the geochemical data after the analyses of the water samples.

HYDROGEOCHEMISTRY

The ground waters from the studied areas in the Mesta River Basin (Table 1) were found to have

Table 1
Results obtained for some major and commonly analyzed parameters

Sample	831-1	831-2	831-3	831-4	831-6	831-7	831-8	831-9	831-10	831-11	831-12	831-13	831-5**
Points*	65	69	74	77	81	82	85	91	93	95	97	100	79
Level, m	921	529	1369	764	534	519	461	725	1655	1671	1174	1404	551
pH	7.6	7.6	7.3	8	8.6	7.7	7.9	8.6	7.7	8.1	8.5	7.4	9.8
T, °C	11.3	11.5	7.0	12	20.5	12	15	13.2	8.6	9.6	9.7	14.1	14
TDS, mg/l	124	165	82	213	246	611	576	323	67	68	251	129	193
TH, meq/l	1.03	0.78	0.43	1.96	2.65	7.16	5.03	3.17	0.40	0.25	2.15	1.10	0.15
EC, μS/cm	147	123	71	218	280	666	605	356	58	57	256	147	283
PO, mgO_2/l	0.64	0.8	0.88	0.72	0.8	0.64	0.72	0.88	0.96	0.8	0.8	0.88	0.96
F^-, mg/l	<0.1	<0.1	<0.1	0.24	0.1	0.1	0.21	<0.1	<0.1	<0.1	<0.1	<0.1	1.27
Cl^-, mg/l	2.7	3.05	1.14	1.23	4.41	2.25	9.39	2.59	1.27	3.66	1.71	3.86	15.17
NO_2^-, mg/l	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05	<0.05
NO_3^-, mg/l	5.59	<0.1	<0.1	0.43	<0.1	<0.1	<0.1	2.54	<0.1	<0.1	1.7	6.58	<0.1
PO_4^{3-}, mg/l	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1	<0.1
SO_4^{2-}, mg/l	10.54	12.1	6.86	9.32	4.63	7.9	13.03	20.04	5.57	3.67	9.55	14.45	12.63
HCO_3^-, mg/l	60.52	57.77	38.51	123.8	170.6	442.9	385.1	203.6	33	30.26	148.5	57.77	96.28
CO_3^{2-}, mg/l	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	<5	2.7
NH_4^+, mg/l	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01	<0.01
Ca^{2+}, mg/l	16.71	11.94	5.45	33.94	43.81	114.5	60.49	53.85	6.39	4.08	37.42	18.46	2.85
K^+, mg/l	2.33	1.34	1.36	0.67	0.74	0.46	5.99	0.88	0.57	1.26	1.96	0.53	0.15
Mg^{2+}, mg/l	2.4	2.29	1.98	3.18	5.58	17.52	24.48	5.89	1	0.58	3.46	2.18	0.11
Na^+, mg/l	4.58	8.53	3.08	5.78	5.84	3.47	31.75	8.29	2.56	4.13	8.25	4.82	51.47
Si, mg/l	6.96	25.08	8.65	7.15	3.71	8.09	16.47	9.19	6.22	7.33	14.14	6.96	12.46
Ca^{2+}/Mg^{2+} ratio	4.2	3.2	1.7	6.5	4.8	4.0	1.5	5.5	3.9	4.3	6.6	5.1	15.7
Na^+/Cl^- ratio	2.6	4.3	4.2	7.2	2.0	2.4	5.2	4.9	3.1	1.7	7.4	1.9	5.2

Note: *65 – Gorno Dryanovo; 69 – Gospodintsi; 74 – Popovi Livadi; 77 – Breznitsa; 81 – Sadovo; 82 – Petrelik; 85 – Hadzhidimovo; 91 – Mesta; 93 – Gotse Delchev; 95 – Treshtenik; 97 – Cherna Mesta; 100 – Avramovo; 79 – Banichan. **Sample taken from the groundwater mineral source of Banichan.

temperatures ranging between 7.0 °C and 20.5 °C and tend to be slightly alkali, with low mineralization, from very soft to hard (Figs 2–4). They were found to be primarily of the calcium-bicarbonate type. The distribution of the calcium and carbonate ions is presented in Figs 5, 6. The hydrogeological units are presented in accordance with the geological map in scale 1:50,000: map sheets Velingrad (Sarov *et al*., 2009a), Hadzhidimovo (Sarov *et al*., 2010b), Gotse Delchev (Klimov *et al*., 2010a), Dobrinishte (Milovanov *et al*., 2009a), and Yakoruda (Sarov *et al*., 2011b). The hydrochemical types of groundwater are presented in Table 2.

According to the accepted in the Republic of Bulgaria and the EU administrative classification of groundwater bodies, eleven groundwater bodies are located in the Mesta River Basin (Fig. 7, Table 3). The monitoring points, where the operative and controlling monitoring of groundwater quality by the Executive Agency takes place, are presented in Fig. 8 and Table 4. In seven of those bodies are located the points from which samples were taken in 2020 (Fig. 7).

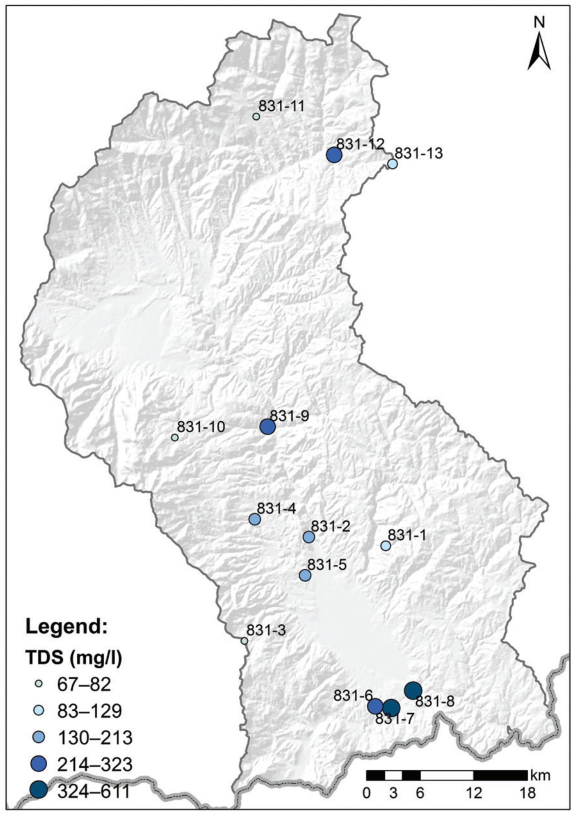

Fig. 3. Total dissolved solids distribution.

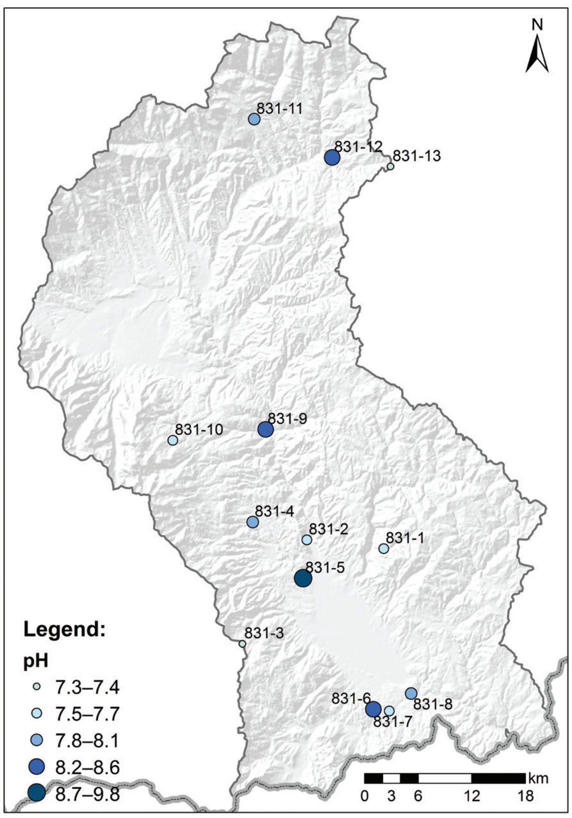

Fig. 2. Hydrogen-ion activity distribution for the Mesta River Basin.

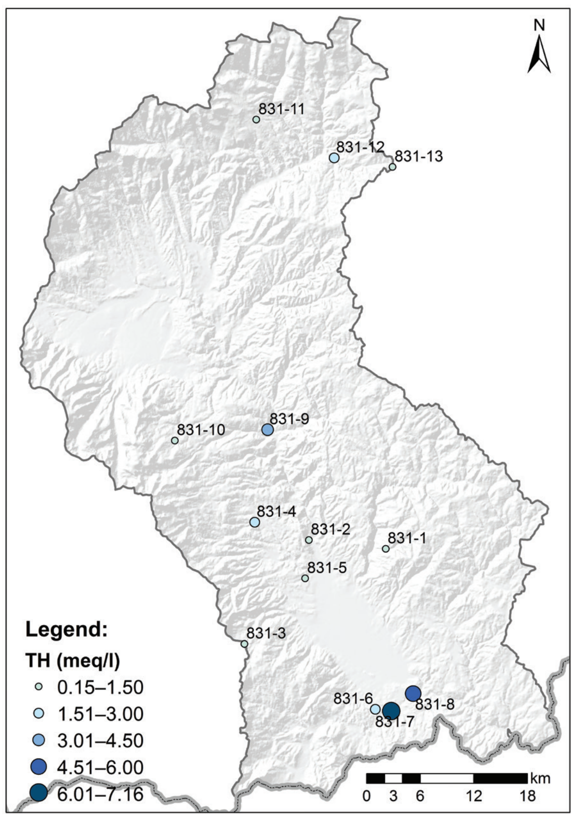

Fig. 4. Total hardness distribution.

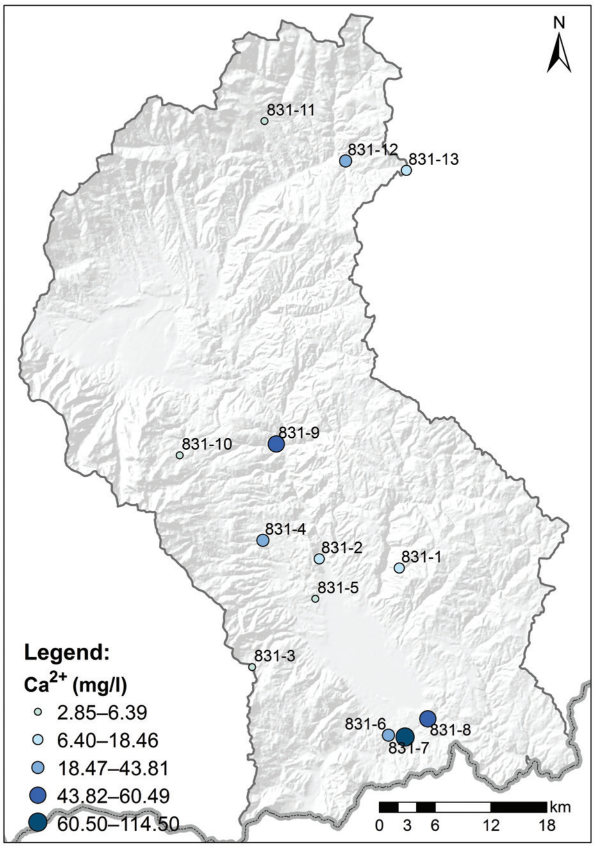

Fig. 5. Calcium distribution.

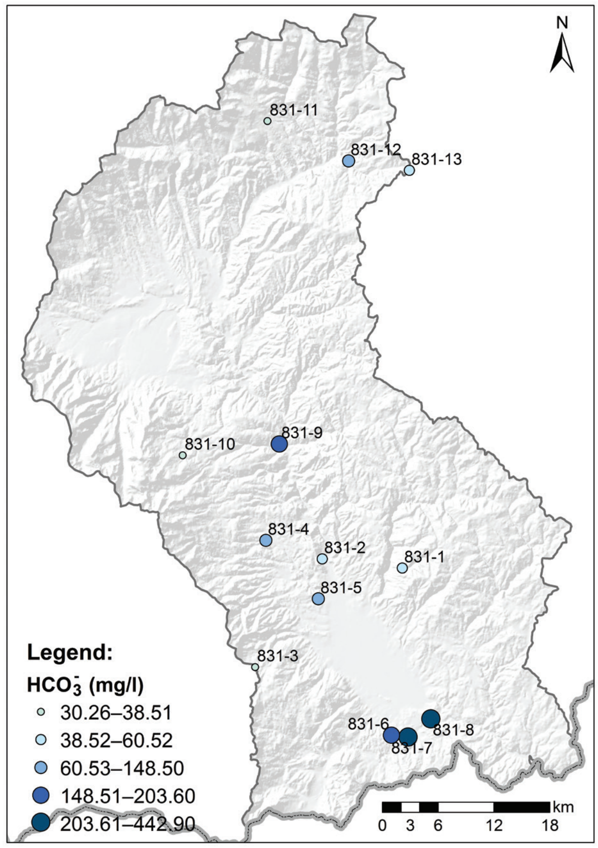

Fig. 6. Bicarbonate distribution.

Ground waters formed in the Precambrian metamorphic rocks (metagranites of the Sarnitsa lithotectonic unit and migmatized biotite, amphibole-biotite gneiss and gneiss-schists of the Slashten lithotectonic unit) were found to be slightly mineralized in the range of 0.124 g/l and 0.576 g/l, with pH between 7.6 and 7.9. The groundwater in the region was found to vary from very soft, with TH = 1.03 meq/l (in Gorno Dryanovo), to quite hard, with TH = 5.03 meq/l (in Hadzhidimovo) (see Fig. 4). According to their chemical characteristics, they can be of calcium-bicarbonate nature (sample 831-1), as well as of calcium-magnesium-hydrocarbonate nature, with an increased sodium contents, 20.98% of the cations or 10.28% of all ions (sample 831-8). The hydrocarbonates were found to be in the range from 60.52 mg/l to 385.1 mg/l (Table 1). The concentration of calcium ions varies between 16.71 mg/l and 60.49 mg/l, and the concentration of sodium ions varies between 4.58 mg/l and 31.75 mg/l.

The ground waters found in Paleogene effusive rocks (dacites and rhyodacites) are mostly of the calcium-bicarbonate type and calcium-sodium-bicarbonate type (Table 2, Fig. 9), with an increased content of sodium (31.13% of the cations or 14.98% of all ions), and sulphate ions (19.62% of anions, and 10.18% of all ions) (sample 831-2). The concentration of calcium ions was found to be in the range from 11.94 mg/l to 53.85 mg/l, and the concentration of bicarbonate ions in the range from 57.77 mg/l to 203.6 mg/l. The sulphate ions were found to be from 9.32 mg/l up to 20.04 mg/l. Sample 831-5 was taken from an abandoned borehole, about 1 km to the west of the road from Gotse Delchev to Bansko, from the mineral water spring near Banichan Village. The collector at the Banichan deposit was found to be composed of volcanics, *i.e.*, dacites, rhyodacites, and rhyolite tuffs, rhyolite xenotuffs, tuff sandstones, and conglomerates (Table 2). This is mineral water with prevalence of nitrogen gas, or the so-called nitrogen weakly mineralized alkaline waters (Petrov, 1964). The mineral water from the Banichan source can be described as having low content of soluble substances. The overall mineralization was found to be 193 mg/l. As to the content of cations, the most prevalent are sodium cations

Table 2
Hydro-geochemistry of the main hydrogeological units

Sample	Age*	Hydrogeological Unit*	Unit*	Water facies
831-1	Precambrian	Precambrian metamorphic rocks with waters in weathering zone and tectonic cracks	Sarnitsa lithotectonic unit (two-mica metagranites)	$Ca\text{-}HCO_3$
831-8			Slashten lithotectonic unit (migmatized biotite and amphibole-biotite gneiss and gneiss-schists)	Ca/ $Mg\text{-}HCO_3$
831-2	Paleogene–lower Oligocene (Rupelian)	Waters in lower Oligocene effusive rocks of the Mesta River Lowland	Dacites and rhyodacites (subvolcanic and extruded bodies)	Ca/ $Na\text{-}HCO_3$
831-4 831-9	Paleogene–lower Oligocene	Waters in lower Oligocene effusive rocks	Rhyodacites Rhyodacites	$Ca\text{-}HCO_3$ $Ca\text{-}HCO_3$
831-5	Paleogene–lower Oligocene	Mineral waters in lower Oligocene effusive rocks of the Mesta Lowland	Volcanic formation (dacites, rhyodacites and rhyolite tuffs, rhyolite xenotuffs, tuff sandstones and conglomerates)	$Na\text{-}HCO_3$
831-3	Paleogene–lower Oligocene	Waters in lower Oligocene intrusive rocks	Teshovo pluton (medium-grained amphibole-biotite granodiorites)	Ca/ $Mg\text{-}HCO_3$
831-10	Paleogene	Waters in Paleogene intrusive rocks	Central Pirin pluton (coarse-porphyric biotite granites to granodiorites, Bezbog type granitoids)	$Ca\text{-}HCO_3$
831-12 831-13	Paleogene Palaeogene (Lutetian?)	Paleogene intrusive rocks with waters in weathering zone and tectonic cracks	Rila-West Rhodope batholith (granites – medium to fine-grained biotite granites)	$Ca\text{-}HCO_3$ $Ca\text{-}HCO_3$
831-11	Paleogene	Paleogene intrusive rocks with waters in weathering zone and tectonic cracks	Rila-West Rhodope batholith (granodiorites – porphyric granodiorites)	Ca/ $Na\text{-}HCO_3$
831-6 831-7	upper Miocene–Pliocene	upper Miocene–Pliocene sedimentary water complex	Conglomerate and sandstone formation (breccia-conglomerates, conglomerates and sandstones)	$Ca\text{-}HCO_3$ $Ca\text{-}HCO_3$

Note: *According to the geological map sheets in scale 1:50,000 (Sarov *et al*., 2009c, 2010a, 2010b, 2011b; Klimov *et al*., 2010b).

(see Fig. 9), and the most prevalent anions are bicarbonate ions. According to its type, the mineral water tends to be of bicarbonate-sodium nature, with bicarbonate ions (69.57%); the contents of sulphate and other anions exceeds 25% (SO_4^{2-} – 11.60%, and Cl^- – 18.83%), whereas sodium prevails over other cations at 93.51%. The water is characterized by high pH = 9.8, low mineralization, and temperature of 14 °C, silicon concentration of 12.46 mg/l, and fluoride content of 1.27 mg/l (Table 1).

The Paleogene plutonic rocks (granites and granodiorites) (Table 2) host groundwater of the calcium-bicarbonate type with a higher number of sodium ions, 21.08% of the cations or 9.12% of the sum total of all ions (for sample 831-10); calcium-sodium-bicarbonate type with sodium ions amounting to 38.72% of all cations, or 15.76% of all ions (for sample 831-11), and with a higher sulphate content (20.58% of anions and 10.79% of all ions) (sample 831-13); calcium-bicarbonate type (sample 831-3) with a higher number of magnesium ions, 27.05% of all cations and 11.60% concentration of all ions, and sodium ions (22.14% of all cations, or 9.49% of all ions). The concentration of bicarbonate ions varies in the range from 30.26 mg/l up to 148.5 mg/l, and the concentration of calcium ions varies from 4.08 mg/l to 37.42 mg/l.

Ground waters of the upper Miocene–Pliocene sedimentary complex (breccia-conglomerates, conglomerates, sandstones) can be described as belonging to the calcium-bicarbonate type (Table 2), varying from soft (sample 831-6) to hard (sample 831-7), with an increased content of magnesium ions, 19.74% of all cations and 9.77% of the concentration of all ions (sample 831-7). The concentration of bicarbonate ions varies from 170.6 mg/l to 442.9 mg/l, and the concentration of calcium ions varies from 43.81 mg/l to 114.5 mg/l. The magnesium ions

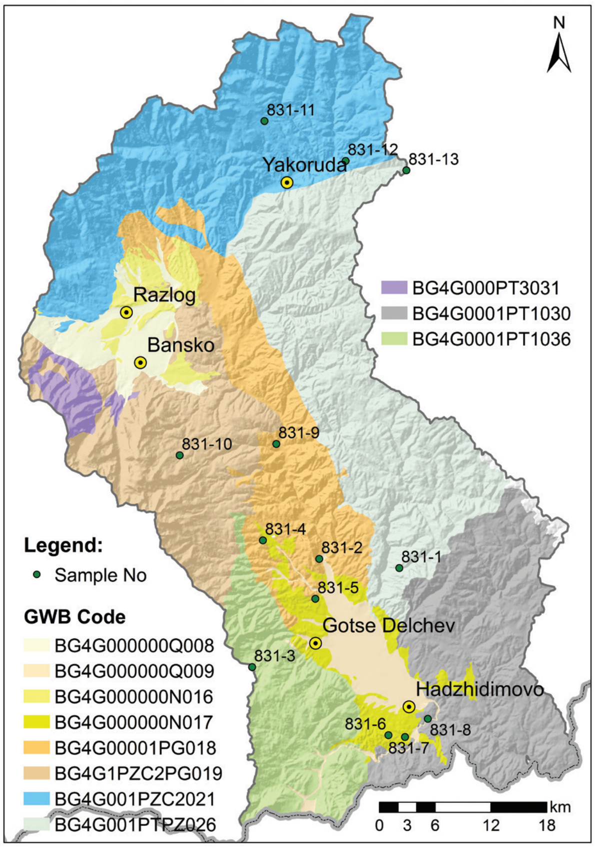

Fig. 7. Groundwater bodies in the Mesta River Basin (according to the River Basin Management Plans of the West Aegean Region).

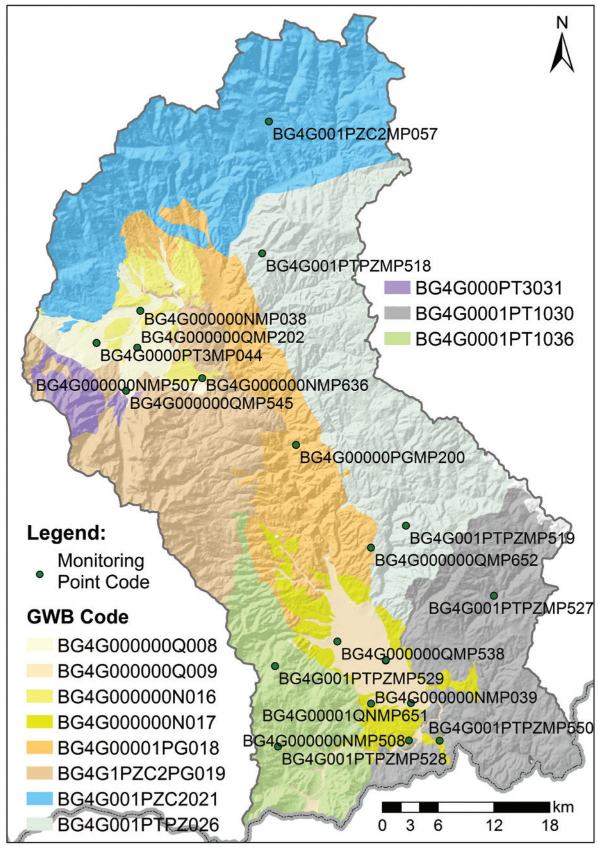

Fig. 8. Groundwater monitoring points and groundwater bodies in the Mesta River Basin (according to the River Basin Management Plans of the West Aegean region).

were found to be in the range between 5.58 mg/l and 17.52 mg/l (for sample 831-7).

From the hydrogeochemical interpretation of water analyses, carried out on the studied samples from the Mesta River Basin, and the Piper Diagram (Piper, 1944), which shows their major ion chemistry, it follows that in the studied samples: *1*) alkaline earth metals (Ca^{2+}+Mg^{2+}) exceed alkali metals (Na^{+}+K^{+}); *2*) weak acids (CO_3^{2-}+HCO_3^{-}) exceed strong acids (SO_4^{2-}+Cl^{-}); and *3*) carbonate hardness exceeds 50%, *i.e.*, prevalent in the groundwater samples were alkaline earths and weak acids (Fig. 9). This fact has also been confirmed by the Chadha Diagram (Chadha, 1999) (Fig. 10). For waters coming from the groundwater mineral source of Banichan, alkalis exceed the alkaline earths, and weak acids exceed the strong acids, while the carbonate alkali exceed 50%, meaning that groundwater is inordinately soft in proportion to its content of dissolved solids. The Chadha Diagram (Chadha, 1999) contributes to the understanding of the basic geochemical processes influencing the quality of groundwater. Twelve of the samples can be defined as Ca-HCO_3 water recharge types, and one of the samples is dominated by an ion exchange (Fig. 10), proving that the base ion exchange is the domineering factor in the formation of groundwater, and leads to an exchange of Ca^{2+} and Mg^{2+}ions from groundwater with Na^{+} and K^{+} ions from the host rock.

For all the studied samples, it can be concluded that the water composition is similar for plutonic, metamorphic, sandstones and volcanic rocks, the only exception being sample 831-5 (Table 5).

The obtained result for the ratio $Na^{+}/Cl^{-} > 1$ (Rajesh *et al*., 2011) testifies of an increased presence of sodium in the groundwater, most likely as a result of silicate weathering, or of ion exchange between sodium from rocks and calcium from groundwater. The ratio $Ca^{2+}/Mg^{2+} > 1$ (Li *et al*., 2018) is indicative of the presence of Ca ions in the groundwater as a result of calcite dissolution (samples 831-3 and 831-8). The ratio $Ca^{2+}/Mg^{2+} > 2$ is indicative of

Table 3
Main hydrogeological units and groundwater bodies

Sample	Point*	Age**	Hydrogeological Unit**	Unit**	GWB Code***	GWB Name***
831-1	65	Precambrian	Precambrian metamorphic rocks with waters in weathering zone and tectonic cracks	Sarnitsa lithotectonic unit (two-mica metagranites)	BG4G001PTPZ026	Fissured groundwater in “South-Bulgarian granites”, “Western Rhodope metamorphic rocks”, Barutin-Buynovo pluton
831-8	85			Slashten lithotectonic unit (migmatized biotite and amphibole-biotite gneiss and gneiss-schists)	BG4G0001PT1030	Fissured-karst groundwater in Satovcha karst basin, Dolno Dryanovo pluton
831-2	69	Paleogene–lower Oligocene (Rupelian)	Waters in lower Oligocene effusive rocks of the Mesta River Lowland	Dacites and rhyodacites (subvolcanic and extruded bodies)	BG4G00001PG018	Porous-fissured groundwater in the Gotse Delchev Paleogene aquifer
831-4	77	Paleogene–lower Oligocene	Waters in lower Oligocene effusive rocks	Rhyodacites	BG4G00001PG018	Porous-fissured groundwater in the Gotse Delchev Paleogene aquifer
831-9	91			Rhyodacites	BG4G00001PG018	Porous-fissured groundwater in the Gotse Delchev Paleogene aquifer
831-5	79	Paleogene–lower Oligocene	Mineral waters in lower Oligocene effusive rocks of the Mesta Lowland	Volcanic formation (dacites, rhyodacites and rhyolite tuffs, rhyolite xenotuffs, tuff sandstones and conglomerates)	–	–
831-3	74	Paleogene–lower Oligocene	Waters in lower Oligocene intrusive rocks	Teshovo pluton (medium-grained amphibole-biotite granodiorites)	BG4G0001PT1036	Fissured-karst groundwater in the Gotse Delchev karst basin and Teshovo pluton
831-10	93	Paleogene	Waters in Paleogene intrusive rocks	Central Pirin pluton (coarse-porphyric biotite granites to granodiorites, Bezbog type of granitoids)	BG4G1PZC2PG019	Fissured groundwater in Pirin block
831-12	97	Paleogene	Paleogene intrusive rocks with waters in weathering zone and tectonic cracks	Rila-West Rhodope batholith (granites – medium to fine-grained biotite granites)	BG4G001PZC2021	Fissured groundwater in “Rila-Rhodope metamorphic rocks”, “South-Bulgarian granites”, Kalina pluton
831-13	100	Paleogene (Lutetian?)			BG4G001PTPZ026	Fissured groundwater in “South-Bulgarian granites”, “Western Rhodope metamorphic rocks”, Barutin-Buynovo pluton
831-11	95	Paleogene	Paleogene intrusive rocks with waters in weathering zone and tectonic cracks	Rila-West Rhodope batholith (granodiorites – porphyric granodiorites)	BG4G001PZC2021	Fissured groundwater in Rila-Rodope metamorphic rocks, South-Bulgarian granites, Kalina pluton

Table 3 *(continued)*

831-6	81	Upper Miocene–Pliocene	upper Miocene–Pliocene sedimentary water complex	Conglomerate and sandstone formation (breccia-conglomerates, conglomerates and sandstones)	BG4G000000N017	Porous groundwater in Neogene-Gotse Delchev Basin
831-7	82				BG4G000000N017	Porous groundwater in Neogene-Gotse Delchev Basin

Note: *65 – Gorno Dryanovo; 69 – Gospodintsi; 74 – Popovi Livadi; 77 – Breznitsa; 81 – Sadovo; 82 – Petrelik; 85 – Hadzhidimovo; 91 – Mesta; 93 – Gotse Delchev; 95 – Treshtenik; 97 – Cherna Mesta; 100 – Avramovo; 79 – Banichan; **According to the geological map sheets in scale 1:50,000 (Sarov *et al*., 2009c, 2010a, 2010b, 2011b; Klimov *et al*., 2010b); ***According to the geological map sheets in scale 1:100,000 (Dimitrova and Katzkov, 1990; Kozhoukharov *et al*., 1990; Marinova and Katzkov, 1990; Marinova and Zagorchev, 1990; Kozhoukharov and Marinova, 1991; Marinova, 1991); GWB – Groundwater Body according to the River Basin Management Plans, West Aegean Region, Mesta River Basin (https://wabd.bg/content/).

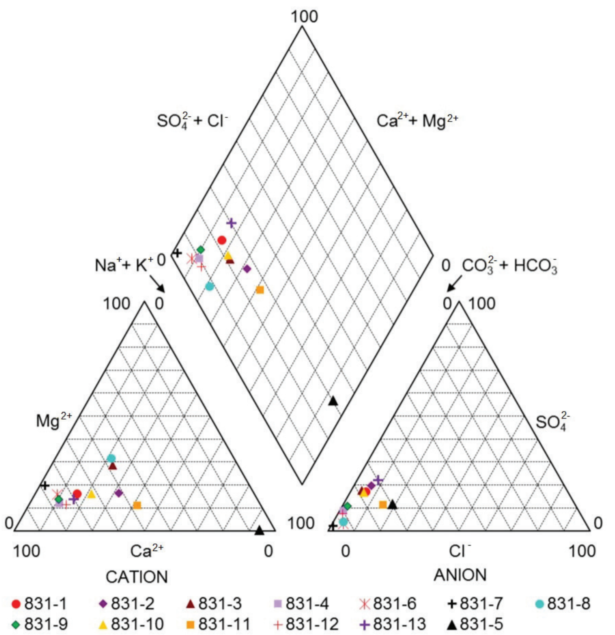

Fig. 9. Water-analysis diagram showing the major ion chemistry according to Piper (1944).

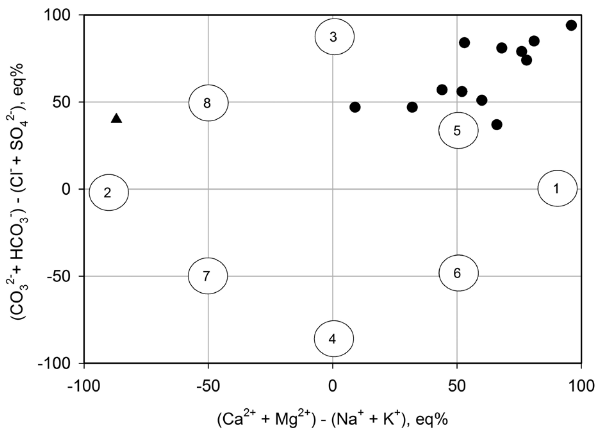

Fig. 10. Diagram showing the major ion chemistry according to Chadha (1999).

silicate mineral dissolution. Silicate weathering is one of the major processes that release Na^+ and K^+ in groundwater from plutonic rocks. With the exception of samples 831-1 and 831-13, all samples showed HCO_3^- > (Ca^{2+}+Mg^{2+}) between the equivalent ion concentrations (Pentchev *et al.*, 1990), proving that waters can be formed by means of in-part dissolution (leaching) of silicate rocks, and contain considerable quantities of sodium and calcium. The only exception is sample 831-5, where the ion sequence in equivalent concentrations HCO_3^- > (Ca^{2+}+Mg^{2+}) shows water formation based on ion exchange of calcium from the liquid phase of sodium from the host rock.

CONCLUSION

The groundwater of the Mesta River Basin can be described as slightly alkali, with pH values ranging between 7.3 and 8.6, and temperatures between 7.0 °C and 20.5 °C. The cation content was established to be in the following order: Ca^{2+} > Na^+ > Mg^{2+} > K^+, and Ca^{2+} > Mg^{2+} > Na^+ > K^+; for the anions, the order is HCO_3^- > SO_4^{2-} > Cl^-. The groundwater mineralization was established as ranging between 67 mg/l and 611 mg/l. The groundwater in the studied area can be described as being from very soft to hard, of bicarbonate nature, such as: *1*) calcium-bicarbonate; and *2*) sodium-bicarbonate (volcanic formations with mineral waters – dacites, rhyodacites and rhyolite

Table 4
Groundwater monitoring points (for controlling and operative monitoring) and groundwater bodies in the Mesta River Basin

X, DD	Y, DD	Location	MP Code	GWB Code*	GWB Name*
23.48206	41.88844	Razlog	BG4G000000NMP038	BG4G000000N016	Porous groundwater in the Neogene (Razlog)
23.5656	41.82564	Dobrinishte	BG4G000000NMP507	BG4G000000N016	Porous groundwater in the Neogene (Razlog)
23.56561	41.82564	Dobrinishte	BG4G000000NMP636	BG4G000000N016	Porous groundwater in the Neogene (Razlog)
23.79959	41.51717	Koprivlen	BG4G000000NMP039	BG4G000000N017	Porous groundwater in the Neogene (Gotse Delchev)
23.85008	41.48287	Petrelik	BG4G000000NMP508	BG4G000000N017	Porous groundwater in the Neogene (Gotse Delchev)
23.48	41.85277	Bansko	BG4G000000QMP202	BG4G000000Q008	Porous groundwater in the Quaternary (Razlog)
23.46778	41.81048	Bansko	BG4G000000QMP545	BG4G000000Q008	Porous groundwater in the Quaternary (Razlog)
23.81639	41.55939	Koprivlen	BG4G000000QMP077**	BG4G000000Q009	Porous groundwater in the Quaternary (Gotse Delchev)
23.81664	41.55983	Dabnitsa	BG4G000000QMP201**	BG4G000000Q009	Porous groundwater in the Quaternary (Gotse Delchev)
23.75322	41.57606	Gotse Delchev	BG4G000000QMP538**	BG4G000000Q009	Porous groundwater in the Quaternary (Gotse Delchev)
23.851	41.519	Hadzhidimovo	BG4G00001QNMP651	BG4G000000Q009	Porous groundwater in the Quaternary (Gotse Delchev)
23.69027	41.76472	Filipovo	BG4G00000PGMP200	BG4G00000PG018	Porous-fissured groundwater in the Gotse Delchev Paleogene aquifer
23.792	41.668	Skrebatno	BG4G000000QMP652	BG4G00000PG018	Porous-Fissured groundwater in the Gotse Delchev Paleogene aquifer
23.88965	41.4837	Petrelik	BG4G001PTPZMP550	BG4G0000PT1030	Fissured-karst groundwater in Satovcha karst basin, Dolno Dryanovo pluton
23.95287	41.62579	Pletena	BG4G001PTPZMP527	BG4G0000PT1030	Fissured-karst groundwater in Satovcha karst basin, Dolno Dryanovo pluton
23.68193	41.47225	Teshovo	BG4G001PTPZMP528	BG4G0000PT1036	Fissured-karst groundwater in Gotse Delchev karst basin, Teshovo pluton
23.67416	41.54984	Delchevo	BG4G001PTPZMP529	BG4G0000PT1036	Fissured-karst groundwater in Gotse Delchev karst basin, Teshovo pluton
23.42706	41.85561	Razlog	BG4G0000PT3MP044	BG4G0000PT3031	Karst groundwater in Razlog karst basin
23.63686	41.9487	Lutovo	BG4G001PTPZMP518	BG4G000PTPZ026	Fissured groundwater in “South-Bulgarian granites”, “Western Rhodope metamorphic rocks”, Barutin-Buynovo pluton
23.83617	41.69053	Kovachevitsa	BG4G001PTPZMP519	BG4G000PTPZ026	(*ibid*., 23.63686)
23.63889	42.07658	Yakoruda	BG4G001PZC2MP057	BG4G000PZC2021	Fissured groundwater in “Rila-Rhodope metamorphic rocks”, “South-Bulgarian granites”, Kalina pluton

Note: MP – Monitoring Point; GWB – Groundwater Body according to River Basin Management Plans, West Aegean Region; *According to the geological map sheets in scale 1:100,000 (Dimitrova and Katzkov, 1990; Kozhoukharov *et al*., 1990; Marinova and Katzkov, 1990; Marinova and Zagorchev, 1990; Kozhoukharov and Marinova, 1991; Marinova, 1991); **Monitoring Point for operative monitoring

Table 5
Cation and anion order in waters draining different genesis rocks in the Mesta River Basin (shown as percentage of cation and anion sum total)

	Ca^{2+}	Mg^{2+}	Na^{+}	K^{+}	HCO_3^-	SO_4^{2-}	Cl^-
Plutonic (granites, granodiorites)	58.41	15.55	22.34	3.69	76.88	14.74	6.72
Volcanic (dacites and rhyodacites)	67.28	13.78	17.51	1.43	83.19	12.99	3.37
Sedimentary (conglomerates, sandstones)	76.47	17.75	5.37	0.4	94.82	2.7	2.48
Metamorphic (metagranites, gneiss and gneiss-schists)	55.3	23.04	18.19	3.47	82.09	9.95	4.69
Volcanic formation*	5.95	0.38	93.51	0.16	70.15**	11.38	18.47

Note: *Volcanic formation with mineral waters (Sample 831-5) – dacites, rhyodacites and rhyolite tuffs, rhyolite xenotuffs, tuff sandstones and conglomerates. **($HCO_3^- + CO_3^{2-}$).

tuffs, rhyolite xenotuffs, tuff sandstones, and conglomerates), where HCO_3^- are the dominant anions, with concentrations of silicon from 3.71 mg/l to 25.08 mg/l. The EC is 57–666 mS/cm. There could not be found any distinguishable groundwater chemistry applicable to any stratigraphic unit. The only exception is sodium-bicarbonate mineral groundwater from volcanic rocks (dacites, rhyodacites and rhyolite tuffs, rhyolite xenotuffs, tuff sandstones and conglomerates). The groundwater mineralization can be described as low, and it does not depend on the type of rocks, meaning the waters are young and of the infiltrating type, actively recharged by precipitation with chloride concentrations of up to 9.39 mg/l.

As far as the Banichan mineral water is concerned, it was found to be of alkali nature, with low mineralization. The cation content is predominantly sodium (93.51%), and the remaining cation content was 6.49%. The bicarbonates, along with carbonates, form 70.15% of the content of sulphate and other anions under 25% (SO_4^{2-} – 11.38%, and Cl^- – 18.47%). The content of cations and anions was found to be in the sequence of $Na^+ > Ca^{2+} > Mg^{2+} > K^+$, and $HCO_3^- > Cl^- > SO_4^{2-} > CO_3^{2-}$. The water is of the sodium-bicarbonate type, and has a high pH = 9.8, mineralization of 193 mg/l, and low temperature (14 °C); the concentration of chlorides is 15.17 mg/l, silicon – 12.46 mg/l, and fluorides – 1.27 mg/l.

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