STUDIA UBB AMBIENTUM, LXVI, 2021, 1-2, pp. 75-88
(RECOMMENDED CITATION)
DOI:10.24193/subbambientum.2021.07

THE QUANTITATIVE AND QUALITATIVE PARAMETERS OF THE BODOC SPRINGS

Melinda VIGH[1*]

[1]Babeș-Bolyai University, Faculty of Environmental Science and Engineering, 30 Fântânele Street, Cluj-Napoca, Romania
**Corresponding author: melinda.vigh@ubbcluj.ro*

ABSTRACT. The post-volcanic phenomena in the Bodoc area are part of the alignment that flanks the western strip of the Carpathian Chain. The fragmented geological structure facilitated the migration of water and gas to the surface. The characteristics of spring water have been studied since the 19th century. On the outskirts of the Bodoc village there are several springs, the most important are Matild, Lenes and Geza. The analysis of water samples was performed in the field (the main parameters) and in the laboratory (major ions). The main water parameters determined in situ where: pH, redox potential, temperature, electrical conductivity, total dissolved solids and salinity, and in the laboratory, where determined the following ions: sodium, calcium, magnesium, ammonia, potassium, lithium, fluorides, chlorides, bromides, nitrites, nitrates, phosphates, sulphates, bicarbonates. The analysis of the parameters shows many similarities, because the springs have the same source or neighbouring sources. At the same time, differences were identified in the case of some parameters, which occurred due to the influence of local factors.

Key words*: spring, post-volcanic phenomena, mineral water, spring flow, physico-chemical parameters.*

INTRODUCTION

Geology

The geological evolution and structure of the area is complex. The emergence of the Carpathian Mountains began in the Mesozoic and continued into the Paleogene. Then, by folding the more friable sediments, was formed the flysch structure. These processes led to the formation of the Bodoc Mountains, where sandstones, conglomerates, marls and clays dominate (Kisgyörgy and Dukrét, 2001).

The structure is characterized by a sequence of anticlines - synclines orientated on the N - S direction. In the depths are hidden a series of horsts and grabens, of which in the studied area are characteristic the Bicsad - Sfântu Gheorghe graben and the Bodoc horst (Airinei and Pricăjan, 1972). To the east stretches a thrust sheet, to the north appears the Harghita area with volcanic eruptions, and to the south are successive blocks of flysch in the form of steps. For the studied area, the Ceahlău thrust sheet is characteristic, consisting of sandstone facieses. Striped clays and friable alluvial sediments have been deposited along the Neogene sandstones along the valleys.

The whole area is characterized by a strong fragmentation. In the western part of the Bodoc Mountains there are two elongated, almost parallel faults, which start in the volcanic area and cross the flysch. These faults facilitated the frequent occurrence of post-volcanic phenomena (Harkó, 1970), see figure 1.

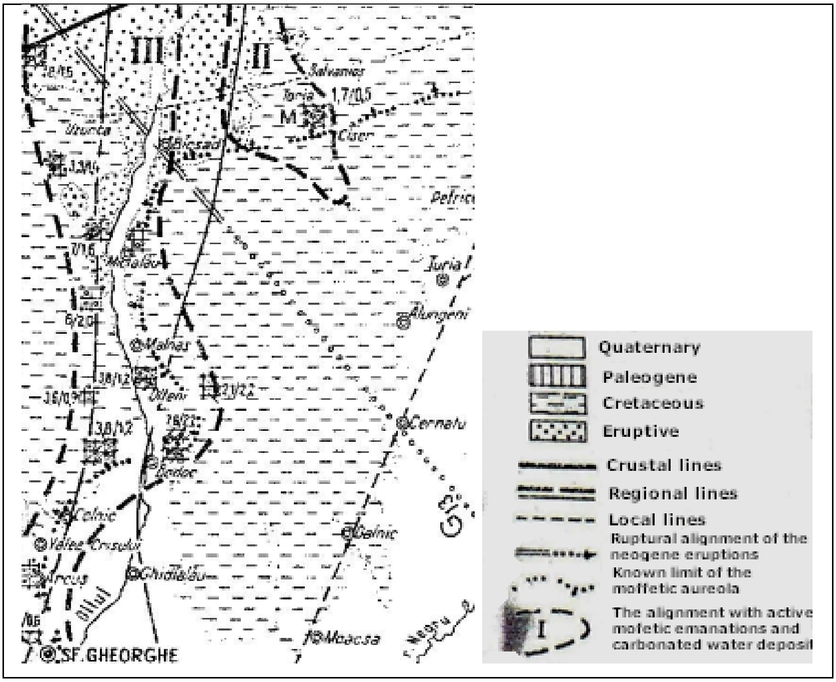

Fig. 1. *Geological structure of the area (after Airinei and Pricăjan, 1972)*

Post volcanic phenomena

The area belongs to a vast mofette aureole located in the flysch formations and Neogene-Quaternary deposits. The post-volcanic manifestations have their origin in the Neogene volcanic activity in the volcanic chain of the

Carpathians Mountains. Dry emanations in the form of mofettes and mineral springs can be distinguished, as a result of the mixture of water in its ascending path among the geological structures with the carbon dioxide of the mofettes. The chemical load of spring water differs depending on the composition of the layers of contact rocks crossed. Thus chloro-sodium, ferruginous, sulphated, chlorinated etc. springs appeared.

Bodoc Deposit

The springs in the area Bodoc are located on the slopes and at the foot of the mountains with the same name, in the eastern part of the commune. The famous traveller and explorer of Transylvania - Orbán Balázs, in his pilgrimages from the 19th century remarked: “at the end of the village, in the valley of the Borviz brook, there is the famous mineral water, which, bottled, reaches Bucharest” (Orban, 1982). There are several sources, the most important are Matild, Géza and Lenes. The first scientific presentation of the waters in the area was made by Hankó Vilmos at the end of the 19th century (Hankó, 1887). 80 years later, Harkó József publishes the first scientific description of these sources (Harkó, 1970). A few years later, Airinei and Pricăjan carried out an extensive study on the mofette aureole in Covasna County, with considerations on the mineral waters from Bodoc. They specify that the post-volcanic activity at Bodoc belongs to the central alignment of the mofette and mineral water deposits area. It extends north to Bicsad - Tușnad, as well as south to Sfântu Gheorghe (Airinei and Pricăjan, 1972).

The springs are fed by the hydro mineral accumulation located in the internal unit of the Carpathian flysch – Ceahlău sheet. In the post-tectonic depression Brașov - Târgu Secuiesc there are two aquifers - one groundwater accumulation, poorly mineralized, and one deep, with high mineralization. The latter is confined to sandstone-conglomerate and sandstone-marl-clay deposits. The migration to the surface of deep deposits is facilitated by the existence of cover faults that furrow the area (Bandrabur and Slăvoacă, 1973).

According to the hydrogeological drilling carried out by the ISP in 1962 and Harkó's study, four hydrogeological complexes were identified:

- a groundwater complex, at a depth of 4.5-9.5 m
- a complex rich in carbon dioxide, between 9.5-16 m
- two deep complexes, located between 20-34 m (Harkó, 1970).

Matild Spring

Matild Spring is the most representative and important source in the area. It is located in the north - eastern part of the village, at an altitude of 594 m. It has been known since the end of the 17th century. It is owned by the village and by the Reformed church. In 1872 it was improved by deepening the spring, equipping it with drainage and building a wooden shelter. It is significant that from the first benefits of capitalizing on water, the village paid a schoolteacher. The Public ownership of the mineral water in Bodoc was then established.

From 1898, the entrepreneur György József started the commercial exploitation of the water from the Matild spring, transporting water by cart to Sfântu Gheorghe, Brașov and Sighișoara, but it reached Vienna and even overseas, where it was very successful (Kisgyörgy, 2008). The first bottling unit was established in 1894 and it operated until 1963 (Feru, 2012). In 1896, at an exhibition that took place in Bucharest, Matild mineral water obtained the gold medal from King Carol I. On this occasion, Victor Babeș also performed chemical analyses on this water. At the Szekler Exhibition of 1905, the mineral water is again awarded the gold medal. During this period, 1500 labelled bottles are already bottled daily, which present the analyses of Hankó and Babeș. In 1922 the Saxon merchant Fleischer rented the spring, from Brașov. The bottling plant is being modernized and increasing its capacity, reaching 6000 bottles in 1948. At the beginning of the 20th century, the original name was changed to Clotild, but it was returned to Matild after 1989. Between 2013-2019, water bottling was stopped. There are currently limited quantities of bottled water on the market.

A hydrogeological drilling was carried out near the Matild spring, under the name Source F 13 RAMIN. Both Matild and F 13 are captured and the water is capitalized through bottling (see in figure 2 the used labels).

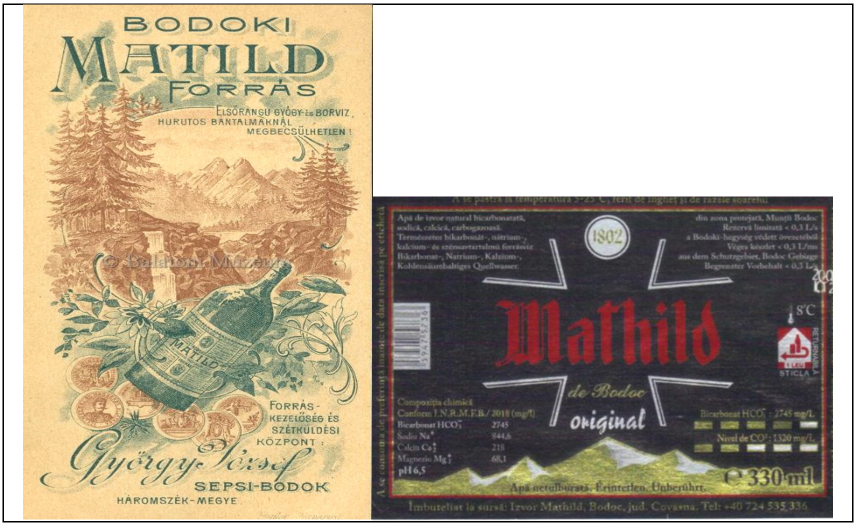

Fig. 2. *The first and current label of Matild bottled mineral water (https://mandadb.hu and https://izvor.ro)*

Lenes Spring

It is located in a garden called Lenes, whence its name. It is much closer to the village, at the foot of the mountains, at an altitude of 551 m. Near the spring there was once a bath called "Veresfürdő / Red Bath". Orbán Balázs, in “The description of the Szeklerland”, mentions the following about this bath: "Above this spring is the Red Bath, which is used for bathing: it’s name comes from the colour of the red deposits, it has beneficial effects for colds and gout" (Orbán, 1982).

Géza Spring

It is mentioned in the Sfântu Gheorghe newspaper as one of the two twin springs, which are located on the western slopes of the Bodoc Mountains (Kisgyörgy, 2008). It is located in the east part of the town, at an altitude of 674 m. It is named after a local enthusiast, who for a long time took care of this spring. It looks like a burst, around which a concrete ring has been built.

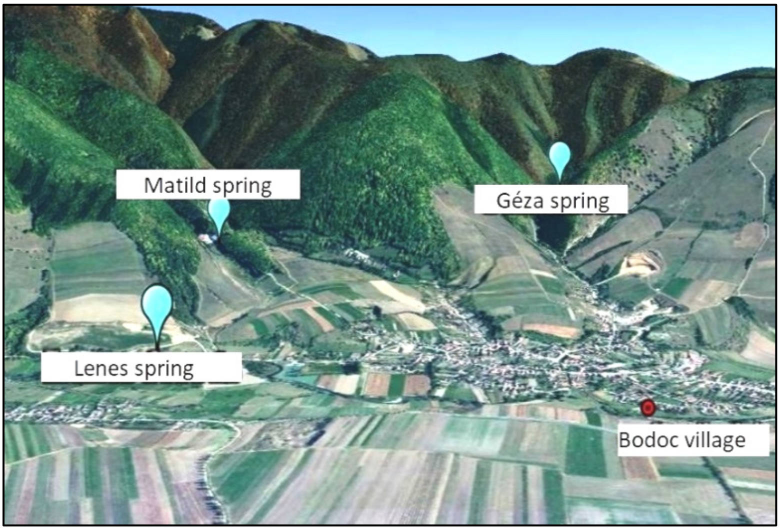

Fig. 3. Location of the springs

METHODOLOGY

The field activity consisted of collecting samples in half-litter bottles, taken from the 3 springs described above (figure 3). Each sampling was repeated three times. Water flow was measured on site with the volumetric method. A WTW 320i Multi-parameter was used in situ, determining the following properties of water: pH, salinity, conductivity, redox potential, total dissolved solids. From the samples collected, were determined in the laboratory the main anions and cations, using a Dionex IC1500; the samples were filtered through a filter (0.45 μS cm) and diluted with ultra-pure water (18 MΩ·cm), until the sample reached a conductivity of 100 μS/cm.

RESULTS

Springs's discharge

The water flow measured at the Matild spring represents only a part of the total source, namely that which is led through a pipe to a well. The captured flow of this spring is of 0.5 l/s, to which is added the flow of Drilling F 13, also 0.5 l/s. If we take into account the amount of water discharge captured and measured, at the Matild spring results a total of approx. 0.64 l/s. Compared to this value, the flows of the others are significantly lower. The discharge from Lenes is only a quarter, and that from Geza is only 12%. At all three sources, the consistency of the water flow in the four months of measurements is noticeable (table 1).

To evaluate the quantitative value of a spring, Kessler introduced in 1952 the notion of water capacity (Gribovszki et al., 2014). The higher the water flow rate, the closer the ratio between the maximum and minimum flow is closer to the unit. At the studied sources, the quantitative capacity is very good, the flow ratio being 1:1.

Table 1. *Springs' discharge (l/s)*

	April	May	June	September
Matild	0.13	0.14	0.14	0.14
Lenes	0.17	0.18	0.17	0.17
Géza	0.08	0.09	0.09	0.08

Temperature. The evolution of the spring's water temperature follows the variation of the air temperature. Thus, temperatures rise until June, and then lower values were measured in October. In all cases, the Lenes spring has the highest temperatures and Geza the lowest. The amplitudes are identical at all three sources (2°C) and are recorded between April and June (table 2).

Table 2. *Water temperature(°C) of the investigated springs*

	April	May	June	September
Matild	10.0	11.5	12.0	11.0
Lenes	12.0	12.5	14.0	13.0
Géza	9.0	10.5	11.0	10.0

pH. The highest values are observed at the Lenes spring, which indicates the increase of bicarbonate content, due to this Lenes spring water is a slightly basic. Here is observed the highest amplitude of values (0.6). At the Matild and Geza springs, the pH values are almost constant and close to the neutral value (table 3).

Table 3. *pH values of the investigated springs*

	April	May	June	September
Matild	7.2	7.6	7.4	7.5
Lenes	8.4	8.0	8.0	7.8
Géza	7.5	7.5	7.5	7.6

Redox potential. Negative values indicate the presence of reduction processes and good water quality. The lowest values are observed at the Lenes spring, and the highest at Matild. The evolution of redox potential over time is not legitimate. The maximum values are recorded in April at Matilda and Geza springs, respectively in September in Lenes (table 4). The minimums are found in April at Lenes, in May at Matilda and in September at Geza. The largest differences are at Lenes spring (29.3 mV), and the smallest at Geza (6.4 mV).

Table 4. *Redox potential values (mV) of the investigated springs*

	April	May	June	September
Matild	-24.4	-44.3	-33.8	-30.5
Lenes	-74.8	-59.5	-58.4	-45.5
Géza	-36.6	-38.2	-37.2	-43.0

Electrical conductivity. The high values from the Matild spring indicate a high concentration of substances dissolved in water. Due to this, the conductivity values are almost double than the normal ones (2500 μS/cm). At the other end is the Lenes spring, where the conductivity is very low. At all three sources the variation of electrical conductivity is relatively small (table 5). At Matild spring the values are almost constant, and the highest amplitudes are observed at Geza (1952 μS/cm).

Table 5. *Electrical Conductivity (µS/cm) of the investigated springs*

	April	May	June	September
Matild	4550	4533	4450	4470
Lenes	512	613	597	575
Géza	3080	2740	1168	3120

Total dissolved solids. At the Matild spring, the concentration of dissolved solids is so high that the device used indicated "above the device limit" (OFL). This is also indicated by the very high water conductivity in this spring. The lowest values are found at the Lenes spring, where there is a remarkable consistency of concentration (amplitude only 66 mg/l). At Geza there is a remarkable parallel with the variation of electrical conductivity. At both springs, parameters' higher values appear in April and September (table 6).

Table 6. *Variation of the total dissolved solids (mg/l) in the investigated springs*

	April	May	June	September
Matild	OFL	OFL	OFL	OFL
Lenes	327	393	363	366
Géza	1970	1751	1747	1997

Salinity. A remarkable constancy of values is observed in the case of the Matild and Lenes springs. The difference is that in the first the values are high, the water being in the slightly salty category, and in Lenes spring the low values puts it in the sweet category (table 7). In Geza spring, the salt concentration values are average and the oscillation is significant (amplitude 1.1).

Table 7. *Salinity (‰) in the investigated springs*

	April	May	June	September
Matild	2.4	2.4	2.4	2.4
Lenes	0.2	0.2	0.2	0.2
Géza	1.6	1.4	0.5	1.6

Cations: Sodium (Na^+), Calcium (Ca^{2+}), Magnesium (Mg^{2+}), Ammonia (NH_4^+), Potassium (K^+), Lithium (Li^+).

Sodium is present in appreciable amounts in the water of the Matilda and Geza springs. The maximum concentrations are 1439 mg/l and 1111 mg/l, respectively, both in October. At these sources, the lowest quantities were measured in June (1085 mg/l and 593 mg/l). Lenes spring is characterized by very small amounts of sodium ions (between 9 - 28 mg/l).

These low concentrations significantly influence the average value, which reaches only 654 mg/l. Excluding the values from Lenes spring, the average reaches almost 1000 mg/l (see figure 4).

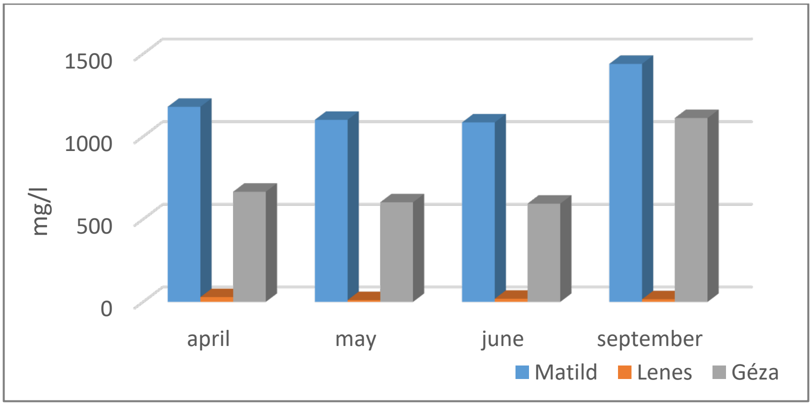

Fig. 4. *Sodium ions variation (in the investigated months)*

The concentrations of calcium are similar in all three springs. Higher values are at the Lenes spring, except in June, when the smallest quantity was measured at this spring. In April, May and October, the amount of calcium in the Matild and Geza springs is almost equal. Absolute extremes were measured at Lenes (79 mg/l in October and 52 mg/l in June). The average of all measurements is 68 mg/l and varies between 71 mg/l at Lenes and 64 mg/l at Geza (figure 5).

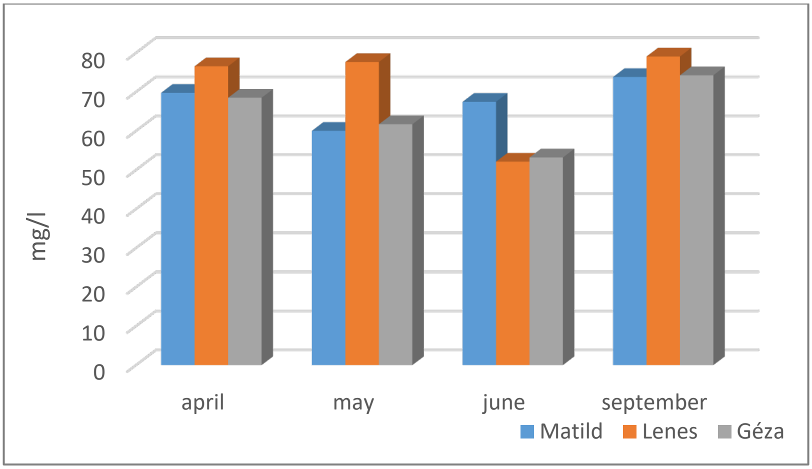

Fig. 5. *Calcium ions variation (in the investigated months)*

Magnesium has a very similar variation as sodium. In each measurement campaign, the highest values were at Matild and the lowest at Lenes. The month with maximum values at all three sources was October. The absolute maximum was recorded at Matild in October (65 mg/l), and the absolute minimum was at the Lenes spring in April (9 mg/l). The highest amplitude - 53 mg/l, was in June (64 mg/l at Matild, 11 mg/l at Lenes). The average of the measurements is 35 mg/l and varies between 54 mg/l at Matild and 13 mg/l at Lenes (figure 6).

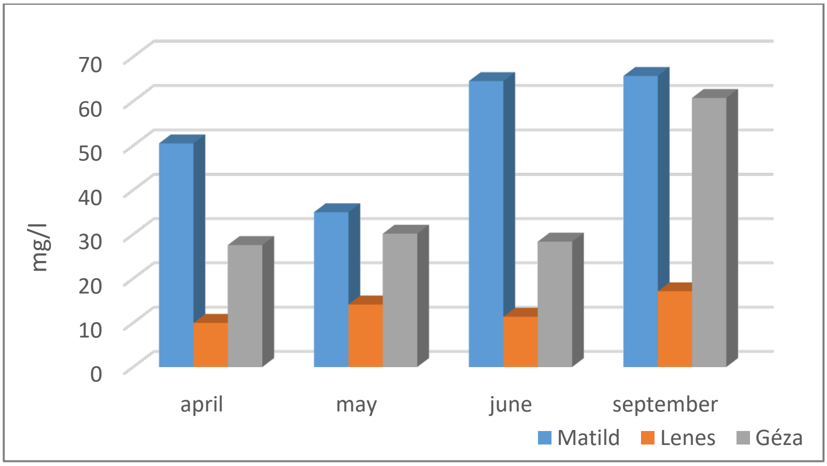

Fig. 6. *Magnesium ions variation (in the investigated months)*

Potassium was identified only at Matilda and Geza springs, in small quantities, and not in all measurement campaigns. Lithium and ammonium could not be identified at any of the three sources, with the used method.

Anions: Fluorides (F^-), Chlorides (Cl^-), Bromides (Br^-), Nitrites (NO_2^-), Nitrates (NO_3^-), Phosphates (PO_4^{3-}), Sulphates (SO_4^{2-}), Bicarbonates (HCO_3^-).

Fluorides registered very high values in April, at the Matild and Geza springs (1.80 mg/l, respectively 1.75 mg/l), which exceeds the limit of 1.2 mg/l according Law no 311/2004, for drinking water in Romania. Otherwise, the values were below 1 mg/l at all sources. The Lenes spring values varied the most, between 0.35 mg/l in May and 0.28 mg/l in October. The absolute minimum value (0.23 mg/l) was at Matild in May. The measurements' average is 0.75 mg/l. The maximum average of 1.01 mg/l was recorded at the Geza spring, and the minimum average at Lenes (0.32 mg/l) (figure 7).

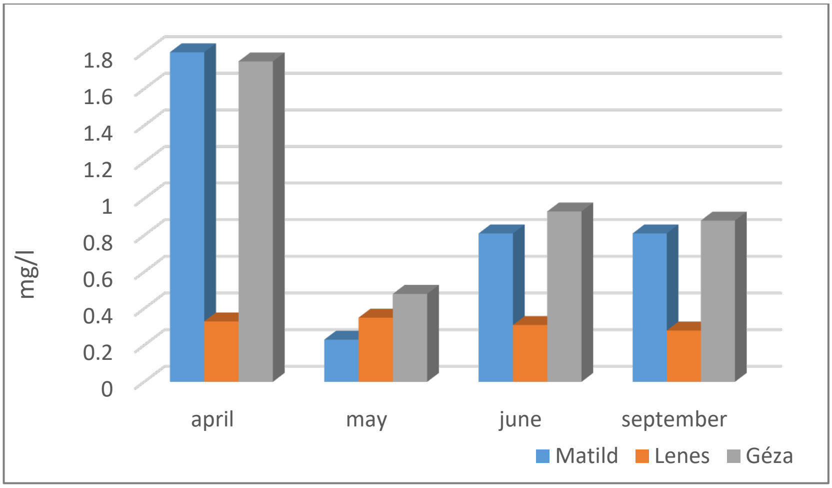

Fig. 7. *Fluorides variation (in the investigated months)*

The variation of chlorides concentration closely follows that of sodium. That is, in the water of the Matild and Geza springs there are much larger quantities than at Lenes. The chloride in the Matild spring is relatively constant, very close to 400 mg/l, in all four months of measurements. This relative constancy is maintained also at the Geza spring, but with lower values (between 143 and 220 mg/l). At Lenes, the chlorides do not exceed 25 mg/l. The amplitude of the extreme values is very high: maximum 427 mg/l at Matild and 14 mg/l at Lenes. The average of all measurements is 200 mg/l (figure 8). The maximum concentration given by 311/2004 law for drinking waters is 250 mg/l.

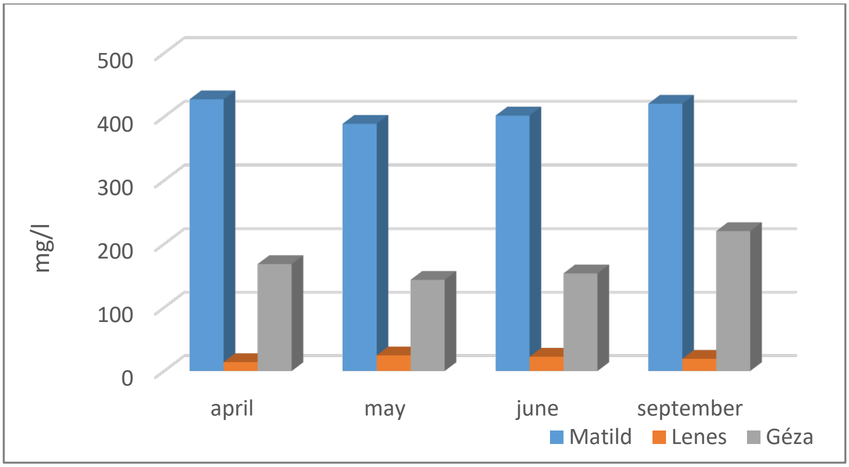

Fig. 8. *Chlorides variation (in the investigated months)*

Nitrates are present in relatively similar quantities at all three springs. Slightly higher values were measured at the Lenes spring. Here is the maximum recorded value of almost 20 mg/l in May. The minimum value, just over 13 mg/l, was registered at the Matild spring in April and October, as well as at the Geza spring in the first three months of measurements. The average nitrate concentration is 15.5 mg/l (figure 9).

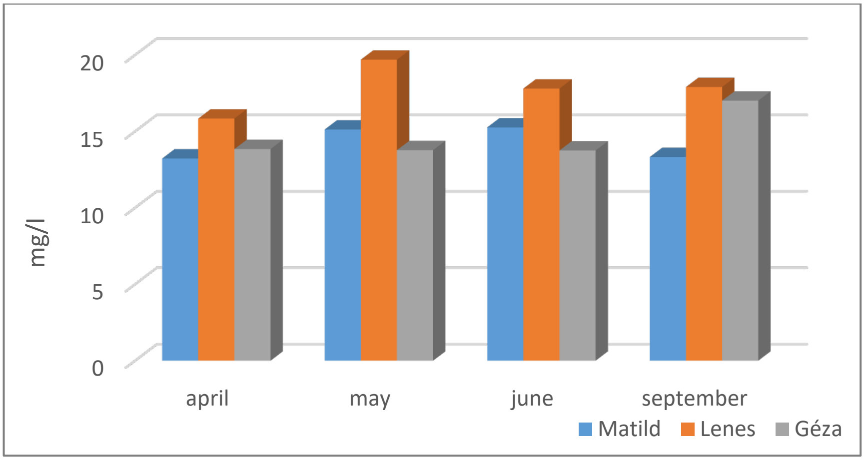

Fig. 9. *Nitrates variation (in the investigated months)*

Sulphates have values above 11 mg/l at the Lenes spring at all measurements and at Geza in June. The maximum of 13 mg/l is at the Lenes spring in June. The concentration in the Matild spring is very constant, with an amplitude of only 0.48 mg/l. The minimum value was measured at the Geza spring in April - 6.5 mg/l. The average of sulphate values is almost 10 mg/l (figure 10).

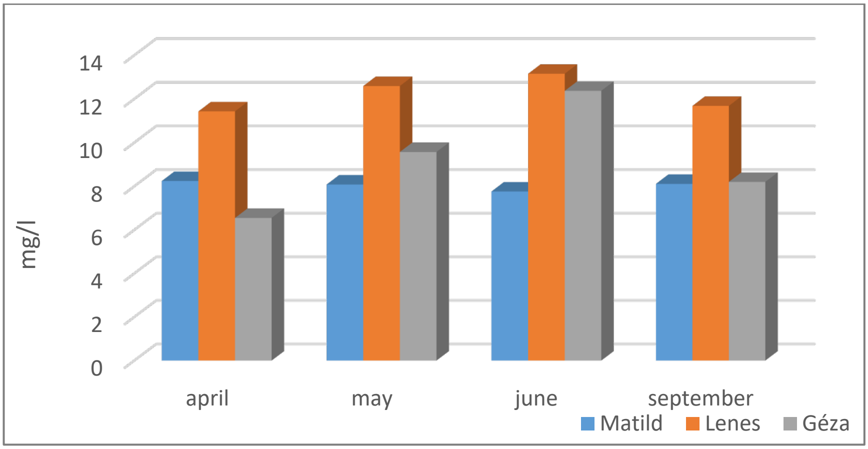

Fig. 10. *Sulfate variation (in the investigated months)*

The concentration of bicarbonates is appreciable at all sources (over 1000 mg/l). Constantly high values, over 1600 mg/l, were measured at Matild. The water from Lenes (640 mg/l) and Geza (415 mg/l) springs has higher amplitudes. The highest value was recorded at Matild in October (1675 mg/l) and the lowest at Lenes in April (1040 mg/l). The average concentration is 1441 mg/l (figure 11).

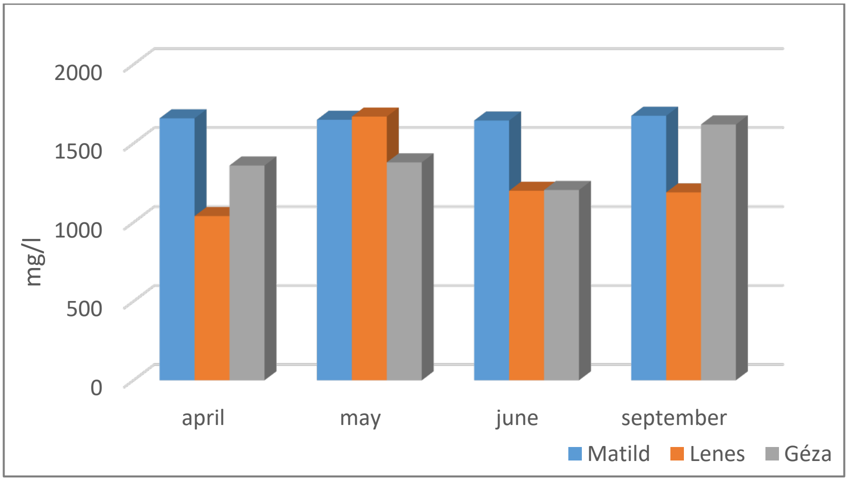

Fig. 11. *Bicarbonate variation (in the investigated months)*

Bromides, nitrites and phosphates could not be identified by the used method on Dionex Ion Chromatograph.

CONCLUSIONS

The mineral waters of Bodoc, currently insufficiently exploited, are an important source, both for food and spa tourism. The physical properties of these waters and their chemical composition indicate a remarkable variety and qualities that must be exploited.

The main source is Matild, which is bottled. There is a remarkable balance in terms of water flow temperature and pH. The concentration of salts and dissolved substances is high. Among cations, sodium dominates with values above 1000 mg/l, calcium and magnesium having values below 100 mg/l. The most important anions are bicarbonates (over 1500 mg/l) and chlorine (around 400 mg/l). These indicators, together with the other components, give Bodoc waters a carbonate – sodium - alkaline characteristic.

Munteanu C. states that alkaline mineral waters are in the form of combinations (chlorine-sodium, carbonated, sulphurous, sulphated, ferruginous, etc.) and joins the waters of Bodoc to those of Sângeorz, Hebe, Slănic Moldova, Malnaș, Karlovy Vary (Munteanu, 2013).

The National Mineral Waters Company through the Exploitation License no. 54/1999 defines the water from the Bodoc perimeter as natural hydrogen-carbonated-sodium mineral water.

Regarding the spa tourism value of these waters, they are recommended for internal cures and aerosols (Teodorescu and Gaceu, 2013).

REFERENCES

Airinei St., Pricăjan A., 1972, Corelații între structura geologică profundă și aureola mofetică din Județul Covasna cu privire la zonele de apariție a apelor minerale carbogazoase. *Aluta*, Sf. Gheorghe, pp. 181-193.

Bandrabur T., Slăvoacă D., 1973, Apele minerale din zona Malnaș – Ozunca*. Studii de hidrogeologie*, București.

Feru A., 2012, Ghidul apelor minerale naturale. Risoprint, Cluj-Napoca.

Gribovszki Z., Kalicz P., Kucsara M., 2014, Víztan, West Hungarian University. Sopron, 240 p.

Kisgyörgy Z., Dukrét L., 2001, Baróti-hegység, Bodoki-havasok. Pallas Publishing, Miercurea Ciuc.

Kisgyörgy Z., 2008, Amiből Mátyás király is ivott*. Háromszék daily newspaper*, Sepsiszentgyörgy.

Hankó V., 1887, Bodoki hideg savanyúvíz elemzése. *Mathematics and Science Bulletin*, M.T.A., Budapest.

Harkó J., 1970, A Málnási és Bodoki borvízek monográfiája. *Tanulmány*.

Munteanu C., 2013, Apele minerale terapeutice, Balneară Publishing, Bucharest.

Orbán B.,1982, republication, A Székelyföld leírása I, II*.* Helikon Publishing, Budapest.

Teodorescu E., Gaceu O., 2013, Turism balnear în România. Oradea Universității Publishing, Oradea.

*** The National Society of Mineral Waters, 1999, Exploitation license no. 54/1999.