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THE MINERAL SPRINGS OF MALNAŞ BĂI

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Abstract. Malnaş Băi is situated in the south of the postvulcanic alignment of the volcanic mountains of the Oriental Carpathians. Underground waters in their way to the surface are strongly charged with mineral salts and gases. So mineral springs appear along the structural faults. It falls into the category of alkaline waters. In Malnaş Băi, the most important spring is Maria, where the water is capitalized by bottling. The other springs lie on another alignment, right in the center of the resort. Quantitative-quality determinations of water have been made since the beginning of the 20th century. At the other springs a measurement campaign was carried out in December 2018. Different parameters were determined on the field and in the laboratory.

Keywords. mineral water, geological structure, hydro-mineral reservoir, spring, parameters, standard deviation, fixed residue.

1. INTRODUCTION

1.1. Physical-geographical conditions

Malnaş Băi is a village in Malnaş commune, Covasna County. It is situated on the right bank of the Olt River, in a depression area, in the eastern extremity of the Baraolt Mountains, at an average altitude of 570 m. The baths are located on the road between Sfântu Gheorghe, 23.4 km south and Miercurea Ciuc, 48.6 km north. The relief in the depression corridor has mild slopes, with heights of 500-800 m. These level differences are due to the succession of the three Olt terraces.

The geological structure of the area is the result of a strong tectonic activity with several major fracture lines. Faults facilitate the lifting of postvulcanic emanations to the surface, which trains the water reserves encountered in the path.

The hydromineral deposit comprises two superimposed aquifers. The lower one is of the Cretaceous age of the fault and fractural type, with marno-limestone deposits (Szekely, 1980). These waters have a strong mineralization. From here comes the most important spring, Maria, as well as the drills 1, 2, 4, 10, 11, 801, 802 used for bottling. The upper aquifer is permeable, of Pliocene and quaternary age, in the deposits of the Olt meadow, with a weaker mineralization. Most springs originate from this aquifer: Ileana, Mioara, Victoria, Padi, Principal, Szemviz, etc., as well as drills 8 and 9. (Munteanu, 2011).

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Harko points out that some of the mineral springs originate from terrace II at 560 m, where andesite blocks predominate, and the other part originates from terrace III at 810 m where the substrate is sand-andesitic (Harko, 1972).

CO_2 emissions are of juvenile origin, which dissolve in ascending water, or come to the surface in the form of mofetta. The carbon dioxide in the presence of water turns into carbonic acid, used in the production of soda, in sparkling wines and in brewing. In the past it was bottled in 20 kg cans, 65 to 70 cans/day. It was considered to be the purest acid in the country, without odor or taste, which was used to enrich other mineral waters in Covasna County.

From bioclimatic research it is clear that temperature, air humidity, wind and atmospheric pressure are the main factors in the location of a special, sparing, sedative-indifferent microclimate. In the resort the temperature is moderate (8°C), with mild winters and cool summers, precipitation is moderate (700 mm) and air mass dynamics is poor (1 - 2 m/s), which gives the place a shelter nature. Under conditions of solar radiation the comfort potential is 60 - 90 days/year.

The water flow, chemical composition of the springs, and carbon dioxide concentration depend primarily on the amount of precipitation and the crossed bed layers. The water flow of the springs in the Malnaş Băi ranges between 0.21 - 0.27 l/sec. (Harko, 1972). The concentration of mineral salts in spring waters is influenced by the layers of rocks that these waters cross in their ascension to the land surface as well as the speed of ascension. At the same time, ascension waters are loaded with different gases, primarily carbon dioxide.

In these conditions the springs have a varied mineralogical composition, which can be used for internal and external cures. The springs have alkaline and salty mineral waters with varying content of carbon dioxide. Due to the curative properties water from the Maria Spring has been redeemed since ancient times, in the form of baths and internal cures.

1.2. Springs

Maria Spring is situated at an altitude of 545 m, and the water is of the artesian type going up from a depth of 156 m. This spring is the most famous due to its very complex mineral composition and beneficial effects on the human body. From a medical point of view, the water of the spring is classified as alkaline (Na, HCO_3) in the slightly salty carbonate subtype (CO_2, Na, Cl) and with relatively low I, Ar, Li, Br, H_3BO_3 and Fe content (Munteanu, 2009).

In the literature, according to author or physician, the water of the Maria Spring is defined differently as alkaline, bicarbonate, chlorine, sodium, carbonate and hypotone, with certain particularities: calcium, magnesium, iodine, ferrous. Due to the high concentration of $NaHCO_3$ and NaCl it is classified as medicinal water.

The 1909 label defines it as "sour, alkaline, natural water, medicinal water spring". The 1926 label mentions "natural alkaline mineral water." On a water bottle for export to Germany is mentioned: "Heilquelle Maria Malnaş natürliche", specifying: "jodhaltiger natrium-hydrogencarbonat-chlorid-sauer". Starting in 2013, it is marketed in ceramic bottles "Malnaş Aqua Telluris", therapeutic water. It is actually the water of the Maria Spring.

The Siculia probe (801) was drilled in 1897 on the Olt terrace, at an altitude of 635m, as additional bottling capacity to the Maria Spring. The depth of the shaft reaches 156 m with a flow of 2500 l/h, and the relative carbon dioxide concentration reaches 97%. In 1899 it was characterized as an alkaline, salty, sour water. In 1904, Dr. Nuricsány József made his analysis: "It is one of the best alkaline salty waters, because the amount of alkali, sodium bicarbonate and salt exceeds internal sources, and even better than foreign sources previously known from a medical point of view "with a water temperature of 12°C. At the beginning of the century, ”Pastilele Siculia” ("Siculia Pills") were patented, where 15 tablets contain as much active salt as one liter of Siculia water (Kisgyörgy, 2009).

Springs from the lower Olt River terrace

They string out along the main road, being designed for public consumption.

Ileana Spring is a bicarbonated, chlorinated sodium water (Jánosi, 2005). It has sour and salty water. At the 2010 measurements by faculty students, the water temperature was 11°C, the flow rate was 0.022 l/s and pH was 8. The Mioara Spring has salty and salty water, with a higher concentration than the water in the Ileana Spring. In 2004, a flow rate of 0.010 l/s was measured, and in 2010 the flow rate was 0.012 l/s, temperature - 10°C, pH - 8. The Victoria Spring is a bicarbonate sodium water with high calcium and chlorine content. The flow is very low, in 2004 it was found dry, and in 2010 it was just dripping. The Main Spring is a bicarbonate, chlorinated sodium water. In 2009, the CO_2 concentration was 1452 g/l and the mineralization was 5512 mg/l. In 2010, the flow was 0.110 l/s and the temperature was 11°C. A label from 1902 was found, the water being referred as dietary mineral water. Szemviz Spring has water rich in sodium, calcium and hydrogen carbonate (Jánosi, 2005). It contains 2.48 mg/l sulfate, 1188 mg/l carbon dioxide. In 2010 the temperature was 17°C and pH - 8.

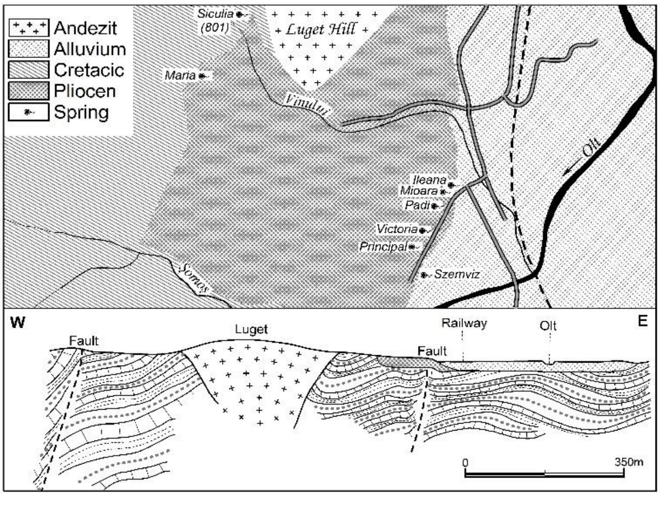

Fig. 1. The geology of the mineral springs area (adapted after Szabó et al.)

2. DATA AND METHODS

The database comes from the literature and from field measurements. Old data have been gathered from books, articles and labels of springs and bottled waters (Maria Spring, Siculia probe). They refer to the concentration of the major anions and cations. Labels are from the years: 1902, 1906, 1926, 1943, etc. Recent measurements were executed in 2004 and 2010. They focused primarily on flow, temperature and pH.

In November 2018, a campaign of measurement was carried out, when the sampling was done in a sunny but cool weather, preceded by rain and snow. The samples of water harvested come from 6 springs: Mioara, Ileana, Victoria, Principal, Szemviz and Padi. The Maria Spring could not be measured because water is captured and used strictly for bottling. Instead, from the concentrations of the ions from the literature, the mean value for the representative ions as well as the standard deviation was calculated, resulting in the final percentage error. The temperature and flow were measured on the spot. In the laboratory, the following parameters were determined with the Consort C933 and WTW 720 multiparameter in the samples: pH, redox potential, ion content, salinity, TDS. Fixed residue was also determined using the instrument Memmert 100-800 oven, glass desiccator and Ohaus AV212CDM balance.

3. RESULTS

3.1. Past information analysis from Maria Spring

The analyzed period ranges from 1943 to 2016, with labels and literature data (Munteanu, Munteanu, 2011). Sometimes values are missing at some parameters, but there is enough data to evaluate the evolutions in good conditions. For a more specific expression, the mean concentration and standard deviation for the years studied were calculated. As a final result, this evolution was expressed as a percentage.

The highest concentration is for the bicarbonates and chlorides. Bicarbonates have the highest values at the beginning and end of the analyzed period. Between them, in 1983 and 1984, the values drop to 3500 - 2300 mg/l. The first two determinations have maximum values: 1943 and 1951 nearly 7000 mg/l. From the mean value (4983 mg/l) there is an error of 28 %.

The concentration of chlorides is much lower but still significant, namely at an average of 1145 mg/l the deviation is 17 %. Here the interval is shorter, only until 2008. The values are more uniform, the oscillations being practically between 1000 - 1500 mg/l. And here the highest values are at the beginning of the interval, with the maximum in 1951: 1535 mg/l. The minimum concentration was in 1978: 964 mg/l.

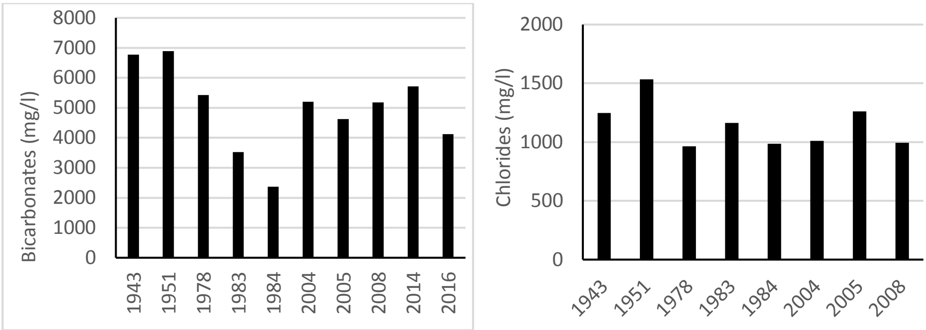

Fig. 2. Concentrations of bicarbonates and chlorates

Among other anions, sulphates have the higher concentration. Although four determinations are missing, it can be observed that the evolution was quite uniform. At an average concentration of 23 mg/l, the error is 18 %. The variation amplitude is 9 mg/l, with a maximum in 1978 (28 mg/l) and a minimum in 1983 (19 mg/l).

Nitrates were determined only in three years. Values range between 10 mg/l in 2004 and 6 mg/l in 1978. The error in these years is 24 %. About bromine are information from five years. Oscillations are high enough to be highlighted by the standard deviation of 2. The maximum was recorded in 1951 (7.3 mg/l) and the minimum in 2008 (2.4 mg/l). Iodine data is five years old. Here we see a progressive decrease in the values, from 2.6 mg/l in 1943 to 0.6 mg/l in 2008. They have the biggest error (51 %) of all the studied anions. Fluoride is present in very small quantities. No value exceeds 0.6 mg/l, but the variation range is small. At an average subunit concentration and error is relatively low of 19 %.

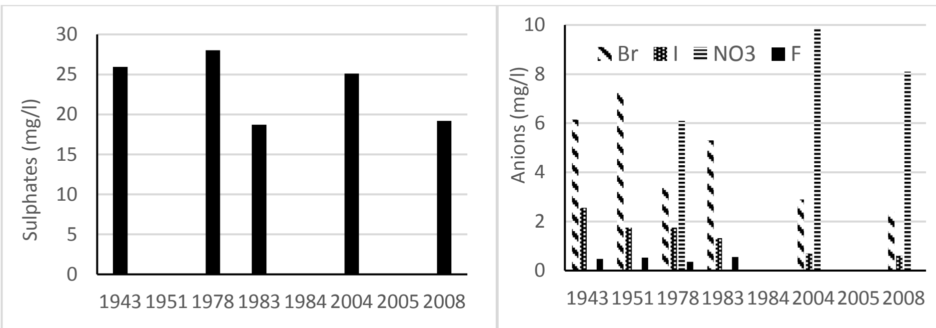

Fig. 3. Concentration of sulphates and other anions

The most important cations are sodium and calcium. Calcium has on average a high value of 200 mg/l, but oscillations are significant with a 38 % error. The maximum amplitude is recorded between 1983 (324 mg/l) and 2016 (55 mg/l). Of the other cations, the highest values are potassium. There is a very good constancy of values (between 67-84 mg/l), although there are three years of measurement missing. Magnesium has a very high value in 1984 (67 mg/l). In the other years the values remain relatively constant, between 20 - 41 mg/l. The mean concentration of

33.33 mg/l has a 41 % error. Lithium was determined only in four years, and concentrations were very low, below 8 mg/l, with deviation being among the smallest (17 %). Similarly, small values are for iron, which in all years do not exceed 10 mg/l, but the deviation is maximum 70 %.

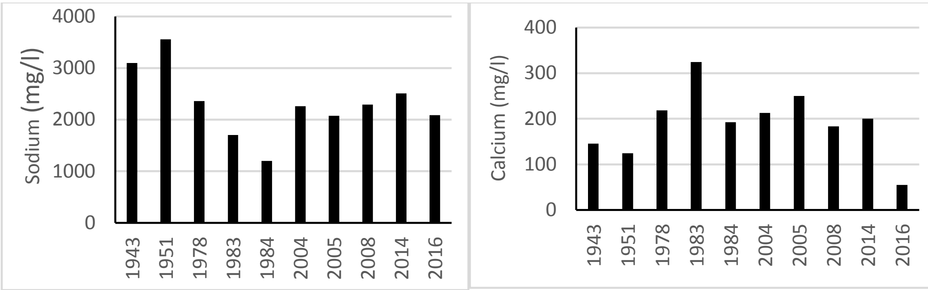

Fig. 4. Concentration of sodium and calcium

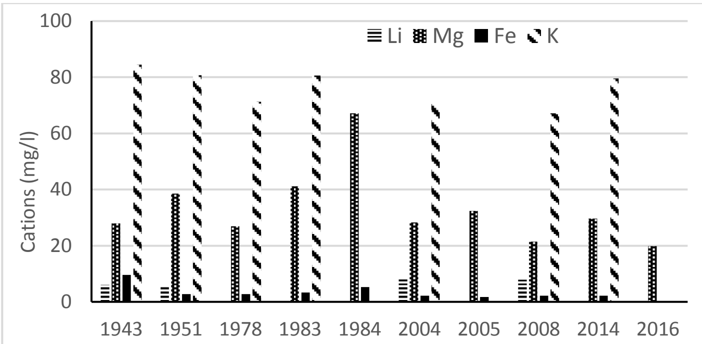

Fig. 5 Concentration of other cations

The other important parameters for the quality of mineral waters are carbon dioxide and mineralization. Both oscillations are not very high. Carbon dioxide is maintained between 1692 - 2440 mg/l. Values of the mineralization degree have a high amplitude of 5914 mg/l, which can be influenced by the number of anions and cations considered, as well as the weather conditions due to the alternation of rainy and dry years. At an average mineralization of 9872 mg/l corresponds a deviation of 21 %.

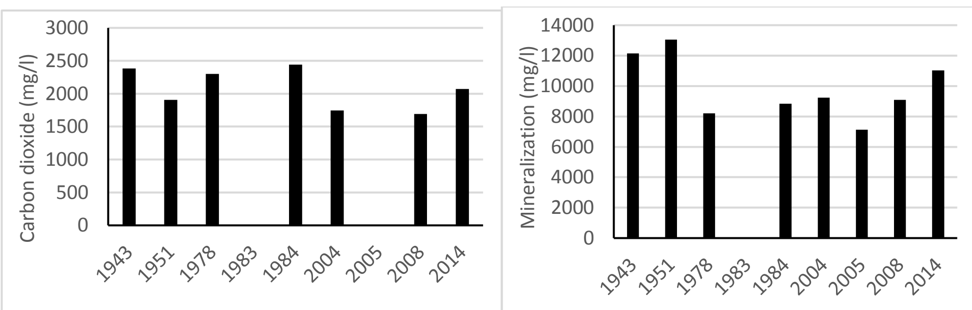

Fig. 6. Concentration of carbon dioxide and mineralization

3.2. Analyzing new data from expedition measurements

The measurements made at the resort show that the flows of the springs are very small. It is worth noting that from this evaluation is missing the Maria Spring, which is captured and cannot be measured in these conditions. Two springs have a slightly larger flow: Padi 63.4*10^{-3} l/s and Principal 62.5*10^{-3} l/s. The lowest flow rate was measured at Victoria, only 3*10^{-3} l/s.

Water temperature is quite different, although the location of the springs is close. The cause may be the different depths from where water comes to the surface as well as the arrangement of springs. Ileana has the coldest water (6 °C), and Szemviz and Padi are the warmest (10 °C).

Table 1. ***Parameters determined on the field***

	Mioara	Ileana	Victoria	Principal	Szemviz	Padi
Temp. (°C)	8	6	7	7	10	10
Flow (l/s)	8.3*10^{-3}	8.9*10^{-3}	3*10^{-3}	62.5*10^{-3}	12.5*10^{-3}	63.4*10^{-3}

Water samples were analyzed in the laboratory with the help of several devices. Six parameters were determined. Concentration of hydrogen ions varies between 7.26 at Mioara and 6.62 at Szemviz. The most alkaline are the sources Szemviz and Padi, with values of 6.62 and 6.64, respectively.

The redox potential reflects the predominance of metal ions at negative values and oxides at positive values. The springs Mioara, Ileana, Victoria and Principal have negative values, with a very large variation (Mioara -23.7 mV, Principal -1.7 mV). Instead, at the Szemviz and Padi springs, the redox potential is positive. Here the values are almost identical (9.6 mV and 9.4 mV respectively).

Concentration of ions exceeds 1000 mg/l at two sources: Szemviz 1430 mg/l and Padi 1460 mg/l. Particularly small is the value at the Mioara Spring, only 419 mg/l.

Salinity greatly reflects the momentary situation and weather conditions through low values that should generally be higher. Because these subunit percentages (max.0.4 ‰) are consistent with the TDS are not considered as an error.

Table 2. ***Parameters determined with multiparameter***

Para-meter	Unit. măs.	Mas. aparat.	Mioara	Ileana	Victoria	Princi pal	Szem viz	Padi
pH		WTW	7.26	6.96	6.88	6.81	6.62	6.64
Redox poten.	mV	WTW	-23.7	- 9.1	- 3.5	- 1.7	+ 9,6	+ 9.4
Ions concentr.	mg/l	C933	419	708	887	925	1430	1460
Salinity	‰	C933	0.4	0.4	0.0	0.2	0.0	0.0
TDS	mg/l	C933	1283	1162	452	883	419	227
Fixed residue	mg/l	Memm ert	2840	4400	1420	2880	1360	760

Dissolved substances are present in large quantities, which reflects the quality of mineral water. Two springs have TDS above 1000 mg/l: Mioara 1283 mg/l and Ileana 1162 mg/l. The poorest water in dissolved substances is the Padi Spring, 227 mg/l.

Fixed residue quantities are also high. In addition to Mioara and Ileana (2840 mg/l and 4400 mg/l respectively), there is a large amount of residue in the Principal Spring (2880 mg/l). As with the TDS, the lowest value was found at the Padi Spring (760 mg/l).

4. CONCLUSIONS

The springs from Malnaş Băi are an important hydromineral source, with multilateral uses. The most important source is Maria Spring, whose capacity was enlarged by the Siculia probe. For a short period, since 1916, the water of the Principal Spring has also been bottled. The other springs have small flows and, although grouped in a tight perimeter, have relatively physico-chemical parameters. Significant values of lithium and potassium are important because the basement is not rich with these elements, and the high concentration is rarer.

The standard deviation presents a wide range of variations between 8 % and 70 %, which puts into question the methodology for obtaining concentrations, especially the old ones that were made in Budapest and Miskolc, and the comparability of data due to the methods used.

The main parameter for determining the mineralization is the fixed residue. According to the Romanian legislation and the European Directives (Feru A., 2012) the values from the sources of the Malnaş Băi springs fall into the category of medium (Victoria, Szemviz, Padi) and rich mineralization (Mioara, Ileana, Principal).

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