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Chemical Changes in Natural Features and Geothermal Well Discharges in Oradea and Surroundings

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ABSTRACT

The Oradea reservoir is an integrated part of the main exploited geothermal reservoir located in the western part of Romania. It is situated almost entirely within the Oradea city, but is hydrodynamically connected with a second reservoir in the Felix Spa resort and 1 Mai resort. Development exploitation of Oradea and surrounding geothermal resources has resulted in changes to the chemistry in natural features as well as of the discharged fluids. In order to monitor these changes, water samples were taken and complete analysed and further used for classifying them and evaluating reservoir behavior through exploitation. A systematic evaluation of the studied geothermal area was done, by using also previous data. The calculated fluid compositions through numerical modeling were compared with the compositions of the wells discharged from the reservoirs.

1. INTRODUCTION

The Oradea geothermal deposit is situated at a depth of 2200-3000 m and occupies an area of 75 km^2 (Cineti, 1990). The geothermal water temperature at the surface is between 70-105 °C. The main uses of the geothermal waters in Oradea consist in the heating of some residential spaces, including the university campus, the provision of sanitary water for housing and administrative spaces, swimming pools, in fish farms. This geothermal reservoir is connected to Băile Felix resort 9 km away from Oradea and 3 km to Băile 1 Mai resort. The thermal waters in Băile Felix and Băile 1 Mai are used for balneary purposes (Şerban and Buhaş, 2014) due to their therapeutic properties known for many years (Ţenu, 1981). In these resorts are natural thermal springs with temperatures of 35-50^{0}C, which constitute a culture medium of the species Nymphaea lotus var. thermalis.

The exploitation of geothermal waters in the area in many swimming pools, followed by the discharging of wastewater into the Peţea rivulet, led to a decrease in the water level of the natural thermal lake "Ochiul Mare" in Băile 1 Mai. Peţea rivulet springs at 8-9 km southeast of Oradea, in the hills of Rontău village, at 140 m altitude. It has sparkling lakes with geothermal waters. The hydrographic network of the Peţea brook is mainly composed of cold surface tributaries: the valley of the Gypsies, the Sky valley, the Rontău and Cordău streams and also of warm affluents: the Lunca brook and the thermal water from the geothermal springs (Ardelean, 1999). In the basin of this rivulet there is the Peţea Peţea Nature Reserve, which was designated the Natura 2000 site (Ilieş et al., 2015).

2. EXPERIMENTAL DETERMINATION

In the attempt to make a connection between the thermal reservoirs operated in Oradea - 1 Mai - Felix basin, several water sampling campaigns were started in the area of interest, aiming to establish their chemical composition (Stănăşel at al., 2002), (Horvath and Şerban, 2016).

In October 2018, the first water sampling campaign took place. In February of 2019, a second water sampling campaign was held.

These water samples were then analysed in the laboratory of the University of Oradea. The analytical methods used for the determination of the main constituents and also for minor constituents and traces are listed in table 1.

Table 1. The applied analytical procedures

Constituent	Method	Equipment	Constituent	Method	Equipment
pH	Electrometric	TitroLine 7750	Na^+ K^+ Mg^{2+} Ca^{2+}	Atomic absorption spectroscopy, direct aspiration	PinAAcle 900T
BO_2^-	Spectrophotometric determination at 420 nm.	UV-VIS SPECORD 210 Plus	Fe^{3+} Al^{3+}	Atomic absorption spectroscopy, graphite furnace	PinAAcle 900T
HCO_3^-	Electrometric titration	TitroLine 7750	TDS	Gravimetry	KERN ABT 220-5DNM
F^- Cl^- Br^- SO_4^{2-}	Ion chromatography	DIONEX AQUION	PO_4^{3-} NO_3^- NO_2^-	Ion chromatography	DIONEX AQUION

The selected sampling points were from Băile Felix, Băile 1 Mai and Oradea. In Băile Felix, water samples were taken from the waterfall pool with Nymphaea lotus var. thermalis (Felix_1), from the outside water collection point next to drilling 4003 (Felix_2), at the water free collection p oint in the yard of the President's Hotel (Felix_3) and from the drilled source of geothermal water that feeds the Aqua President (Felix_4). From Băile 1 Mai, water samples were taken from Perla complex (1Mai_1) water supply drilling, from the Peţea brook at the intersection to the village of Rontău, near the lake of the Natural Reservation (1Mai_2) and from a thermal well drilled to the entrance of Băile 1 Mai (1Mai_3). From Oradea, samples were taken from the Nymphaea Lotus complex (Oradea_1), from the Expoflora greenhouse (Oradea_2), from geothermal water which supplies the central campus of University of Oradea (Oradea_3), from Ioşia (Oradea_4), and two drillings from Sântandrei (Oradea_5) and (Oradea_6).

3. RESULTS AND DISCUSSIONS

The results of the chemical analyses carried out on the samples taken in the two campaigns were processed for the chemical characterization of the waters from the Oradea- 1 Mai -Felix geothermal reservoir. In table 2 you may notice that the pH of the studied water is slightly basic. The highest values are recorded for waters from 1 Mai. Mineralization is high for samples from Oradea 1-3, being above 1 g/l, but in samples Oradea 4-6 there are mineralizations close to those of Felix and 1 Mai, about 0.5 g / l.

Table 2. Results of pH and mineralization of water samples

Sample	pH		Mineralization, mg/l	
	Oct.2018	Feb.2019	Oct.2018	Feb.2019
Felix_1	7.29	7.16	494.6	480.4
Felix_2	8.04	7.11	467.6	491.0
Felix_3	7.48	7.13	463.7	487.9
Felix_4	7.07	7.44	493.2	455.4
1Mai_1	7.68	7.34	397.3	409.9
1Mai_2	8.27	8.04	307.7	543.5
1Mai_3	7.90	7.74	461.3	493.9
Oradea_1	7.80	7.25	1266.9	1248.4
Oradea_2	7.08	7.02	1104.4	1088.2
Oradea_3	7.20	7.18	1231.8	1198.0
Oradea_4	7.78	6.89	478.8	719.7
Oradea_5	8.00	7.20	561.2	559.0
Oradea_6	7.70	8.50	583.5	575.0

Concentrations in bicarbonate ions (Figure 1, Figure 2) obtained by automatic titration led to values ranging from 400-500 mg HCO_3^-/l in waters from Felix. Concentration decreases to 300-400 mg HCO_3^-/l in waters of 1 Mai. The decreasing trend continues to Oradea up to values of 200-300 mg HCO_3^-/l, a slight increase being registered in Oradea 5 and 6. It was recorded a fluctuation in bicarbonate concentration in Felix_2 source and Oradea_6 in the samples from February compared to October.

Concentrations of the other anions in the water (fluoride, chloride, bromide, sulphate, phosphate, nitrate, nitrite) were obtained by ion chromatography. The calibration curves for the anions are shown in figure 3. Chloride content is very low in all studied samples. Sulphate is generally lower than bicarbonate, except waters from sources 1 to 3 from Oradea, where were recorded very high concentrations.

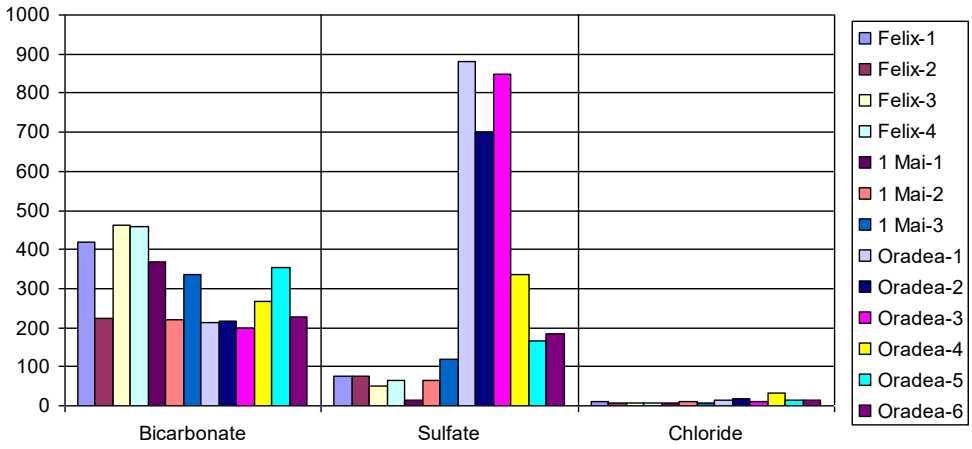


Figure 1: Major anions_October 2018, in mg/l.

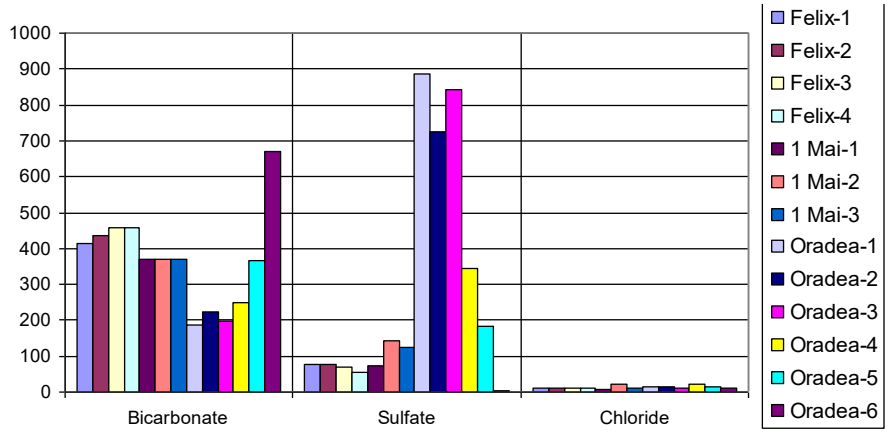


Figure 2: Major anions_February 2019, in mg/l

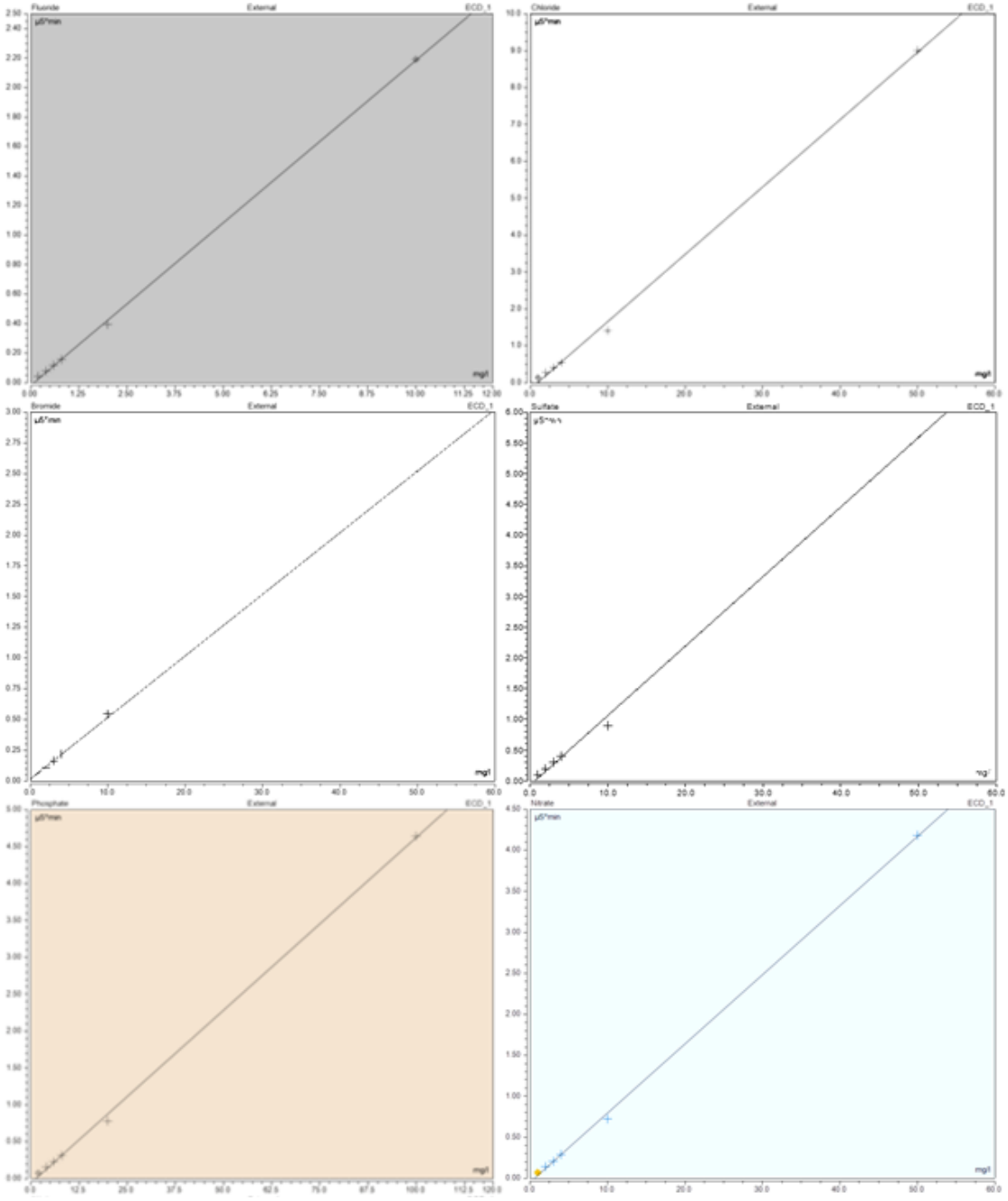


Figure 3: Calibrations curves for anions

A classification based on the majority anions presented in geothermal waters was made using the triangular diagram of Giggenbach (Figure 4). The position of the points within the triangle is obtained by summing the concentrations of the three components, in mg/l, followed by the percentage calculation: % Cl, % SO_4 and % HCO_3. (Giggenbach, 1991) It is confirmed that most waters are peripheral waters with high bicarbonate content, while waters from three wells from Oradea are steam heated waters with high sulphate content.

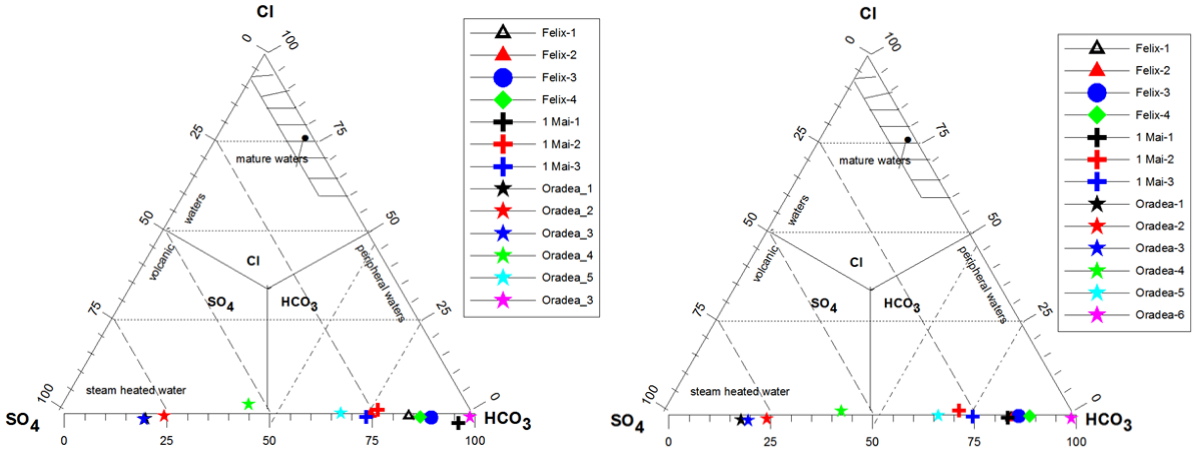
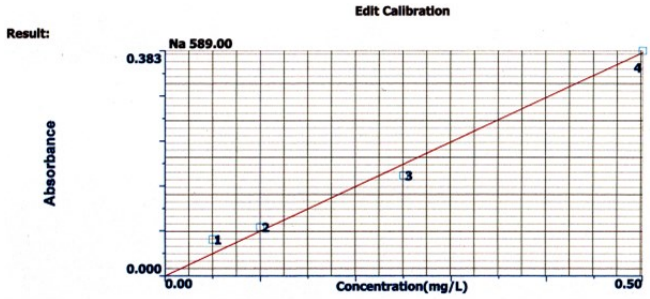
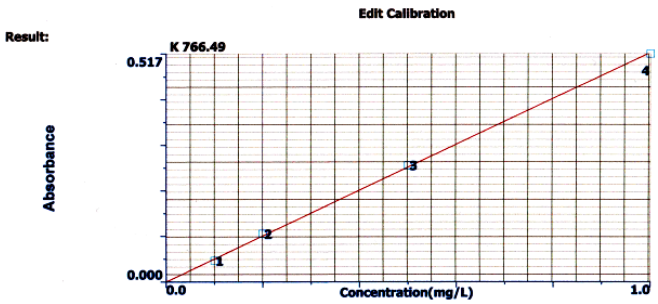


Figure 4: Cl-SO_4-HCO_3 classification of thermal waters in October 2018, respectively February 2019

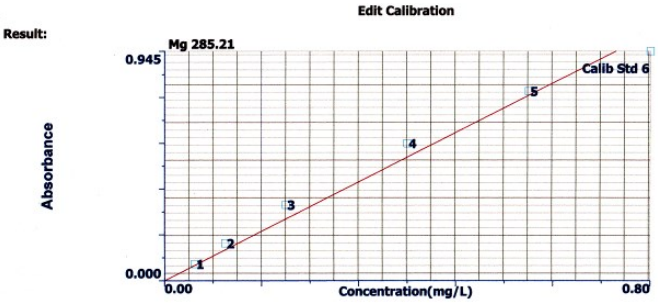
Water cation analysis was performed by atomic absorption spectrophotometry, based on the calibration curves plotted for each type of cation, using standard solutions prepared from standard 1 g/l solutions. Selected calibration curves are presented in figure 5. The results of main cations are presented in figures 6, 7.



Curve correlation coefficient 0.992882



Curve correlation coefficient 0.999765



Curve correlation coefficient 0.990947

Figure 5: Calibration curves for several cations

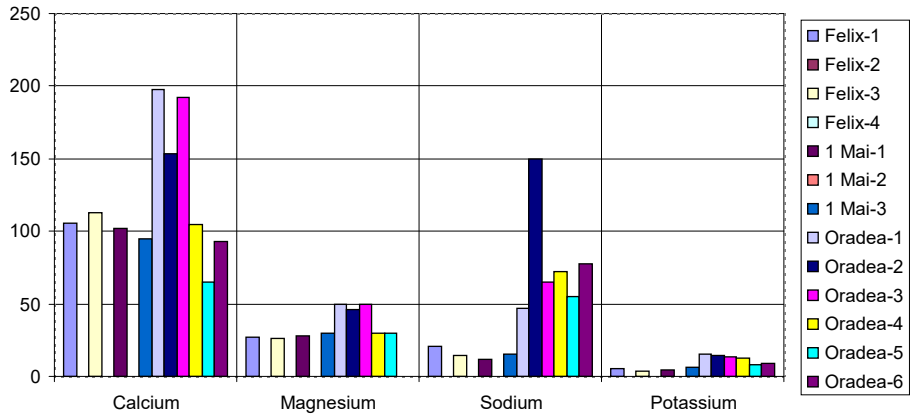


Figure 6: Major cations_October 2018, in mg/l.

The calcium concentrations determined in the studied waters are around 200 mg/l. Concentrations of magnesium ions in water are around 20 mg/l in Felix, 1 Mai and Oradea, locations 4, 5 and 6, but in Oradea locations 1, 2 and 3 are almost 50 mg/l. Sodium concentrations are 10-20 mg/l in Felix and 1 Mai, and in Oradea the concentrations increase to 50-100 mg/l. Concentrations of potassium ions in water are reduced, generally between 3 and 6 mg/l, values exceeding 20 mg/l being recorded in Oradea (figures 6, 7).

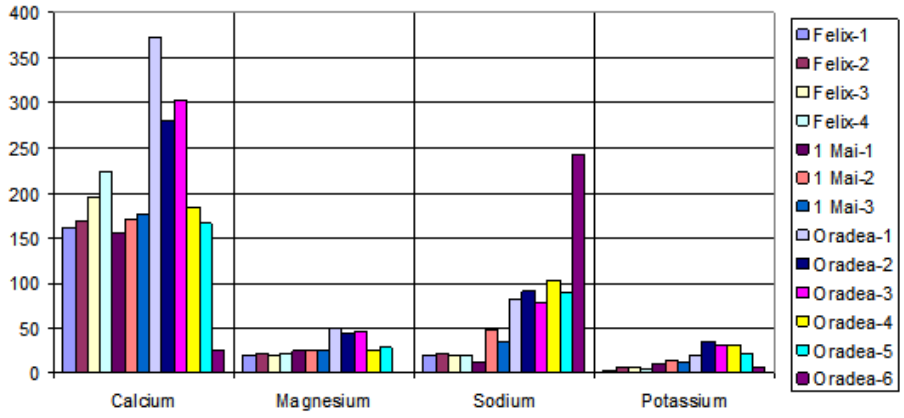


Figure 7: Major cations_February 2019, in mg/l.

From the viewpoint of the majority cations, Na-K-Mg ternary diagrams were constructed (Giggenbach, 1991), (Arnorsson et.al, 1985), summing the concentrations of these cations in mg/l, divided by 1000 for Na, by 100 for K, and ½ for Mg respectively, and then calculate the percentage of each. These are shown in Figures 8, 9.

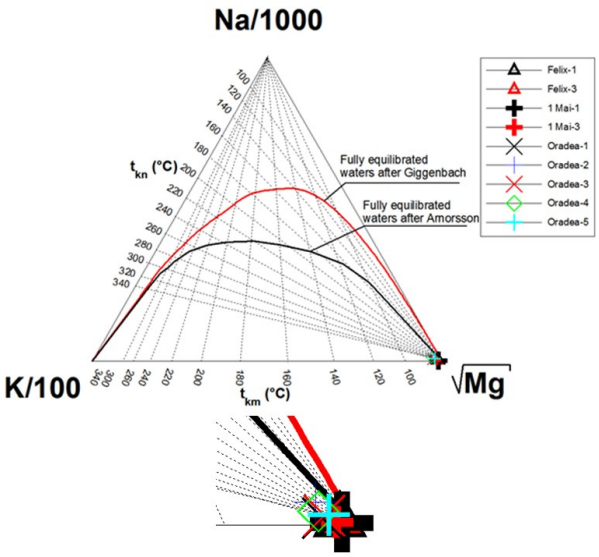


Figure 8: Equilibrium diagram _October 2018

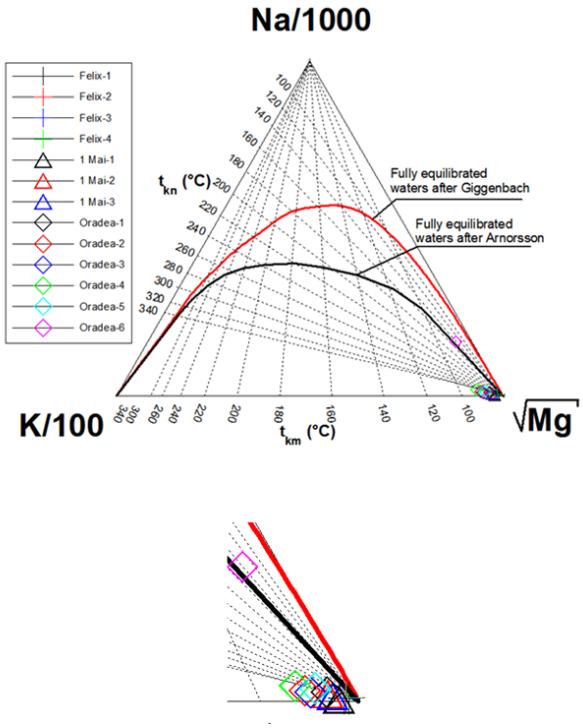


Figure 9: Equilibrium diagram_February 2019

From the Na-K-Mg ternary diagrams, the studied waters are partially balanced, being close to Arnorsson's equilibrium curve. The sample from Oradea 6 is balanced according to Arnorsson's studies. Partial equilibrium may be the consequence of fluid reactions with the rocks that they penetrate or could be the result of mixing water from different temperature zones.

Considering the results of the main anion and cation analyses from the studied waters, based on the Schoeller diagram (Figure 10), it can be observed that the waters have chemical compositions falling within the same characteristics, the difference being recorded on the sulphate ion. It can be appreciated that in February the chemical characteristics are closer to those in October.

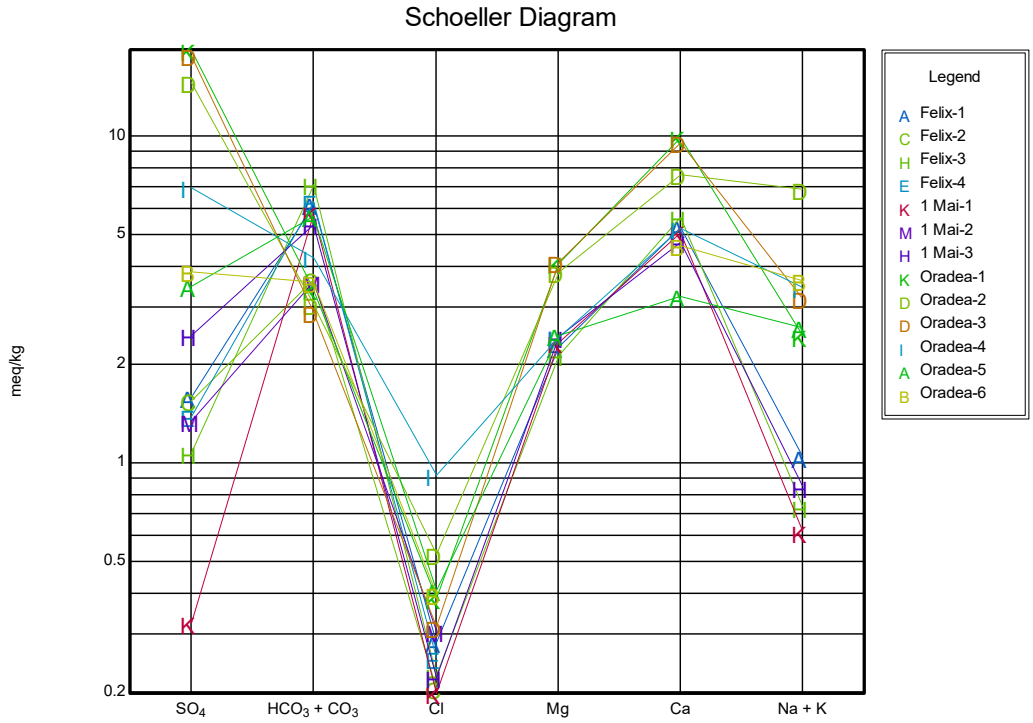


Figure 10: Schoeller diagrams from October 2018

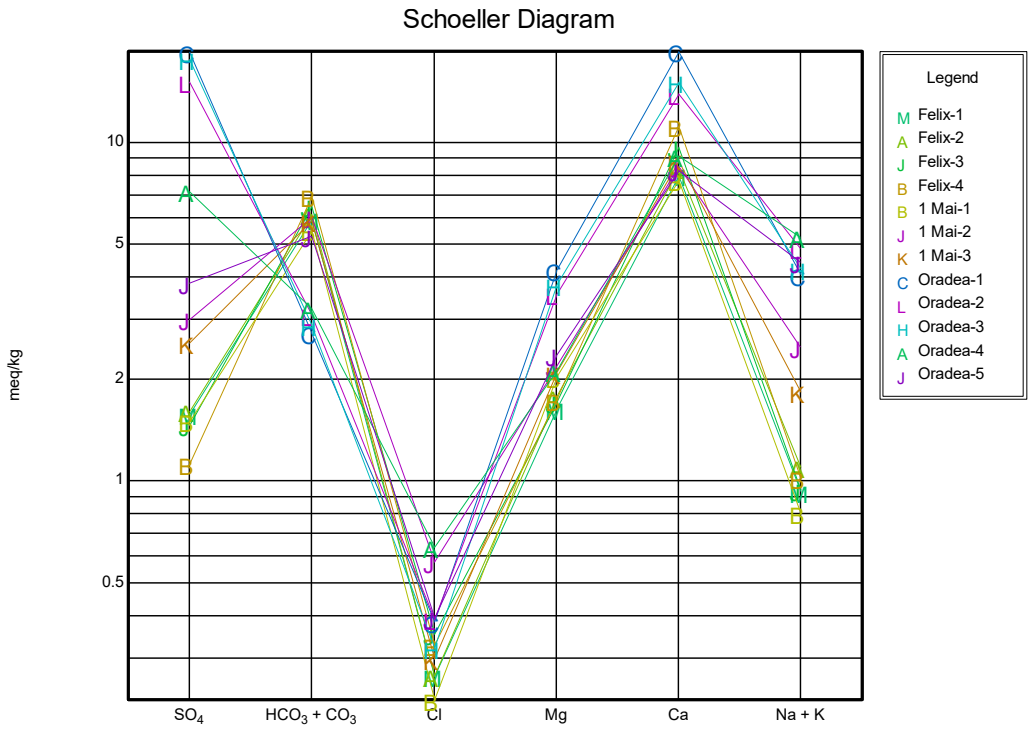


Figure 11: Schoeller diagrams from February 2019

The presence of fluoride ion in all studied waters was found in slightly higher concentrations in February samples (Figures 12, 13). It was also possible to detect the presence of aluminium in traces in all samples in February, in figure 12 the values resulting by multiplying 1000 times its concentration. Trace concentrations have also been found for iron, boron and undesirable presence of bromide and nitrate in water, the latter being in higher concentrations in the waters of Felix, 1 Mai and Oradea in places which provide water to the pools (Figures 12, 13). It is possible to infiltrate in the soil waters from the spill, which mix deeply with the water that comes to the surface.

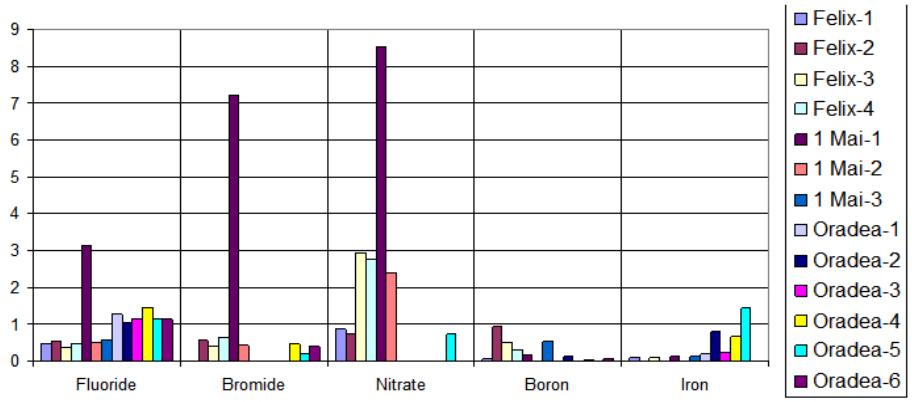


Figure 12: Minor and trace ions_October 2018, mg/l.

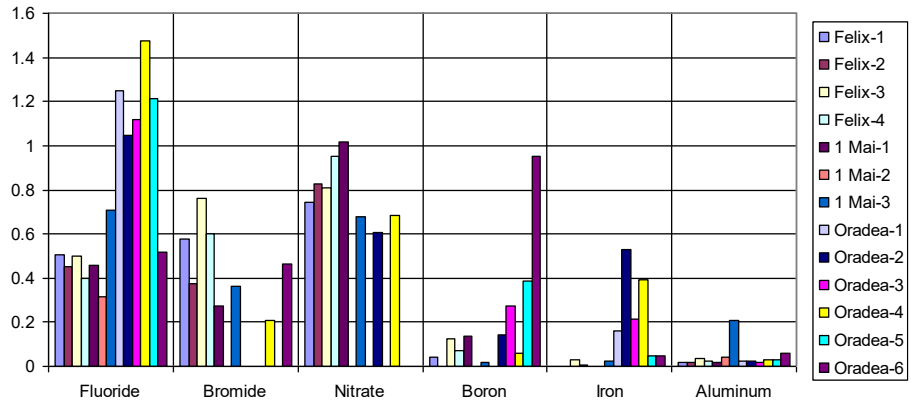


Figure 13: Minor and trace ions_February 2019, mg/l

4. CONCLUSIONS

From the chemical point of view, the studied waters can be classified as calcium-bicarbonated, with the exception of three sources in Oradea, which are sulphated-calcium-bicarbonated.

Bicarbonate is dominant in all analyzed water samples. There is a decrease in the bicarbonate content from Felix to Oradea, Felix samples having concentrations of 400-500 mg/l, those from 1 Mai of 300-400 mg/l, and those from Oradea of 200-300 mg/l, except for locations Oradea 5 and Oradea 6, where the concentrations are over 300 mg/l. Concentrations of chloride ions in water are very small, ranging from 10 to 30 mg/l. Regarding the concentrations of sulphate ions in water, there is a variation starting at concentrations below 100 mg/l in Felix, keeping it below this value in 1 Mai, and at the entry into 1 Mai to Oradea the concentration of sulphate starts to rise to 700-800 mg/l in Oradea, sampling points 1, 2 and 3, and in the other locations in Oradea the concentrations decrease again within the limits of 100-200 mg/l. Phosphate was not detected in the water samples. The presence of nitrite fortunately was not found.

Calcium is the main cation presented in the water samples. Magnesium concentration values are around 20 mg/l, but in sampling points 1_3 from Oradea goes up to 50 mg/l. Sodium concentrations are lower in Felix and 1 Mai compared to Oradea and increase starting by waters from Felix, then 1 Mai and getting maximum value in Oradea_2 in October, while in February, Oradea_6. Concentrations of potassium ions in water are low, 3 to 6 mg/l, values exceeding 20 mg/l being recorded in Oradea.

4. ACKNOWLEDGEMENTS

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