

# Conservation and protection of ecosystems endangered by lack of thermal and freshwater in crossborder area eMS Code: ROHU29



CHEMICAL MONITORING OF ROMANIAN STUDIED AREA  
within  
“Conservation and protection of ecosystems endangered by lack of  
thermal and freshwater in crossborder area” project

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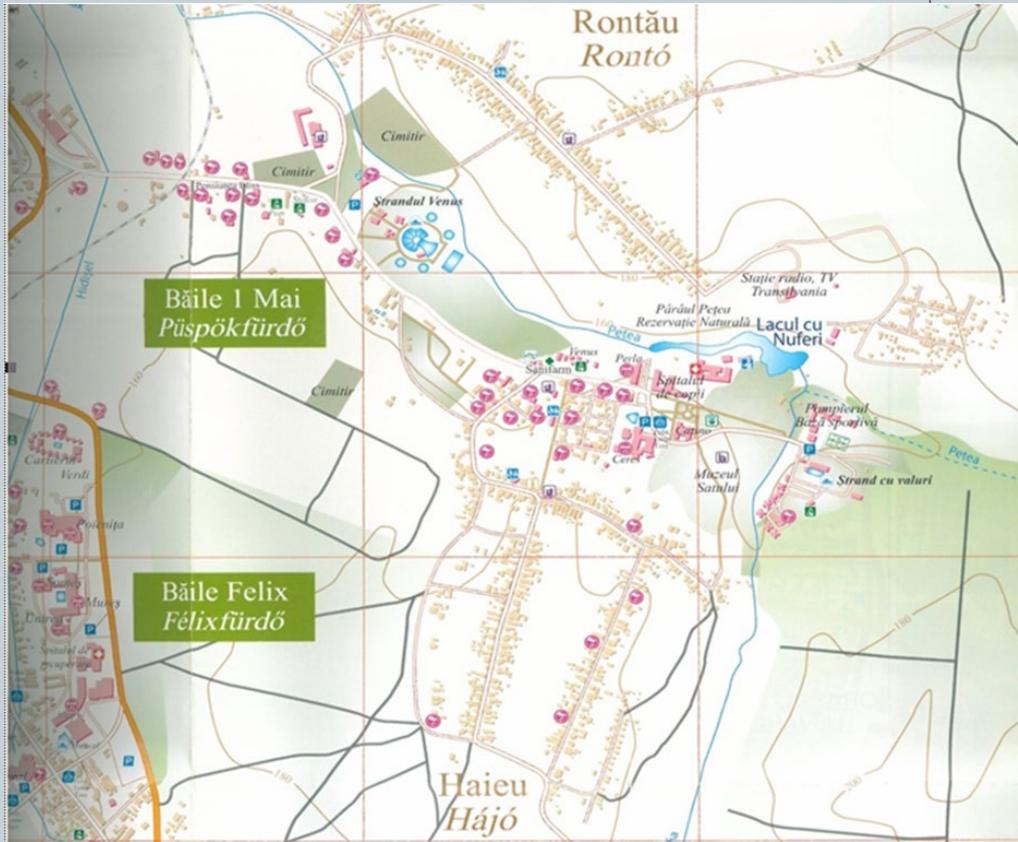
**RESULTS AND DISCUSSIONS**

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# SAMPLING

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## Map of main sampling area



## The need of sampling preservation

- to maintain the sample stability and inalterability of all its constituents from sampling until analysing
- to avoid salts precipitation on the surface of container
- to avoid reactions which lead to variation in the valency of elements by oxydation or reduction processes
- to avoid microbe activity which may cause alteration of analytical parameters
- to avoid any release or absorbtion of substances which may alter the sample composition
- the need of perfect sealing, especially for the samples taken for volatile constituents

## What to analyze from water?

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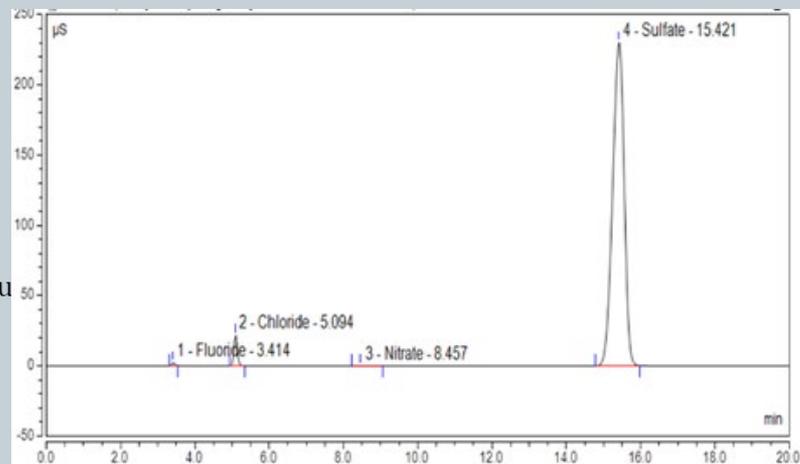
- Fluids properties depend mainly on the mineral rocks the fluid is passing through surface and on the temperature.
- The dissolved components of the geothermal fluid which are determined in the laboratory or in situ, during sampling, can be divided in the following groups, depending on the concentration range:
- **Major dissolved components** - their concentration is about hundred mg/l and more (usually:  $\text{Na}^+$ ,  $\text{Ca}^{2+}$ ,  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{HCO}_3^-$ )
- **Minor dissolved components** – concentration of a few mg/l (usually: F, Br,  $\text{NO}_3^-$ , Fe, Li)
- **Trace dissolved components** – concentration in range of  $\mu\text{g/l}$  (B, Zn, Cu, Pb, Cr, Mo)
- **Gaseous components** – which can include:  $\text{CO}_2$ ,  $\text{H}_2\text{S}$ ,  $\text{O}_2$
- **Radioactive elements:** dissolved gas: Rn, dissolved ions as U, Ra

# Methods of analysis

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- Good analytical results depend on the methodology adopted according to the concentration of the constituents.
- The detection limit (D.L.) is the lowest quantity of a substance that can be distinguished from the absence of that substance (a blank value).
- The relative standard deviation (RSD) is widely used in analytical chemistry to express the precision and repeatability of an assay.
- By *Ion-Chromatographic* method can be analysed simultaneously the anions:  $F^-$ ,  $Cl^-$ ,  $NO_2^-$ ,  $Br^-$ ,  $NO_3^-$ ,  $SO_4^{2-}$ ,  $PO_4^{3-}$ .
  - eluent: 0.0028M  $NaHCO_3$  and 0.00225M  $Na_2CO_3$  solution

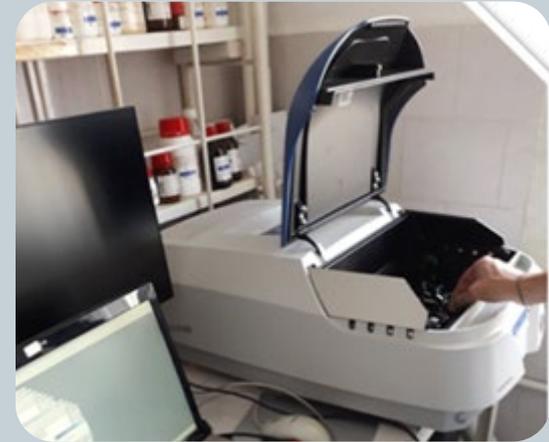
- **Chloride**
  - Titration
  - Indirect AAS determination
  - Ion chromatography – good results
- **Fluoride**
  - Ion selective electrode – good results
  - Indirect spectrophotometric determination
  - Ion chromatography – reasonable, depending on elu
- **Sulphate**
  - Gravimetric - for high concentration
  - Titration – for medium concentration
  - Ion chromatography – good results



# Methods of analysis

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- **SiO<sub>2</sub>**
  - Spectrophotometric method, in VIS – good results
  - AAS
- **Boron**
  - Titration – insensitive
  - Spectrophotometric method, in VIS – good results
  
- **Na, K, Li**
  - Flamephotometry – rather good
  - Atomic absorption spectroscopy –direct aspiration (AAS DA) – very good
  - Inductively coupled plasma (ICP) – very good
- **Ca, Mg**
  - Titration with EDTA solution in presence of murexid as indicator at pH 12-13 and in presence of eriocrom black T at pH 10 – good for high concentrations
  - Atomic absorption spectroscopy –direct aspiration (AAS DA) – very good
  - Inductively coupled plasma (ICP) – very good



# Methods of analysis

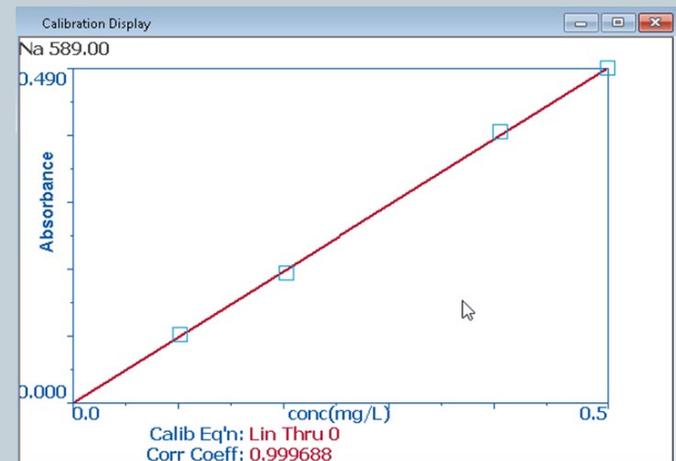
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- **Fe**
  - Spectrophotometric determination at  $\lambda = 510$  nm; samples are treated with phenanthroline, which move the equilibrium to formation of ferrous ions, resulting a red complex – reasonable results
  - Atomic absorption spectroscopy –graphite furnace (AAS GF) - good results for very low concentration
  - Inductively coupled plasma (ICP) – good results
- **Al**
  - Spectrophotometric determination – not sensitive enough
  - Atomic absorption spectroscopy –graphite furnace (AAS GF) - good results for very low concentration
  - Inductively coupled plasma (ICP) – good results
- **Cu, Zn, Cd, Ni, Co** –traces
  - Atomic absorption spectroscopy (AAS) – very good
  - Inductively coupled plasma (ICP) – very good
    - **Isotope analysis:**
      - Deuterium and  $^{18}\text{O}$  in water,
      - $^{13}\text{C}$  in dissolved bicarbonates
        - Mass spectrometry – good results

# Methods of analysis

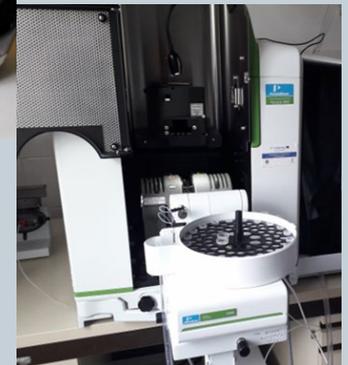
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- A series of standards are run of the element under analysis and a calibration curve is constructed by plotting the concentrations of the standards against the absorption. The curve corrector is set to read out the proper concentration.
- The samples are aspirated and the concentrations are determined directly or from the calibration curve. Standards must be run each time a sample or series of samples is run.



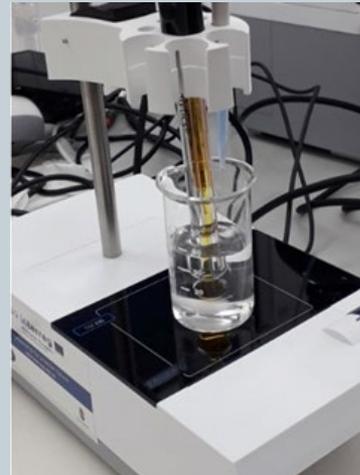
# Methods of analysis

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# Methods of analysis

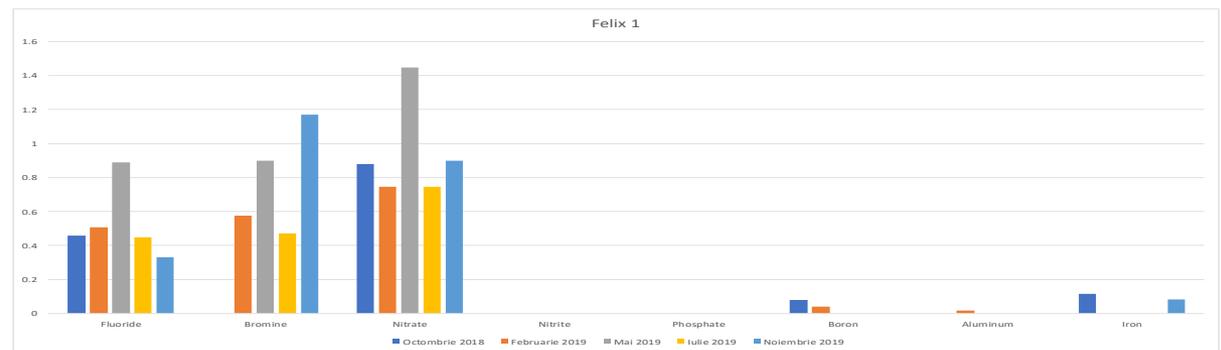
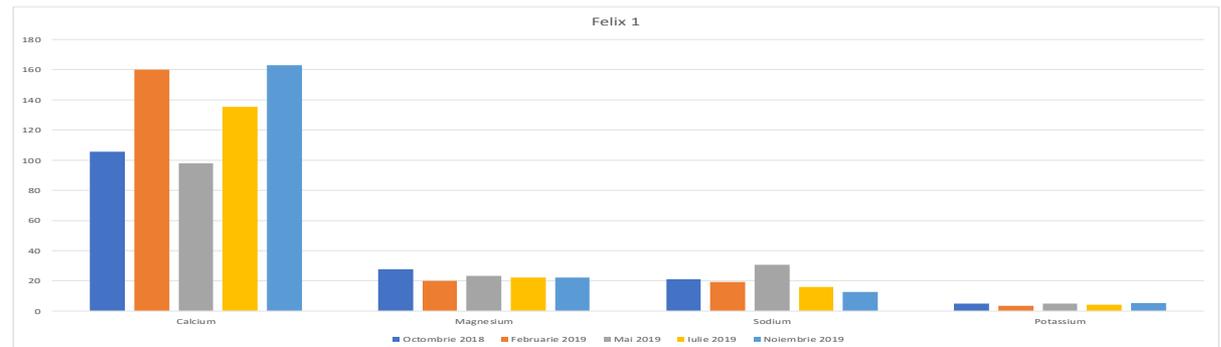
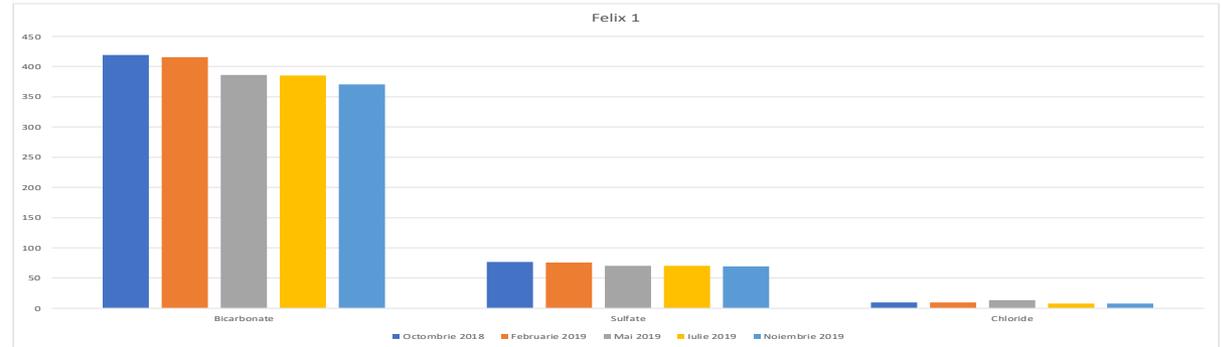
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## RESULTS AND DISCUSSIONS

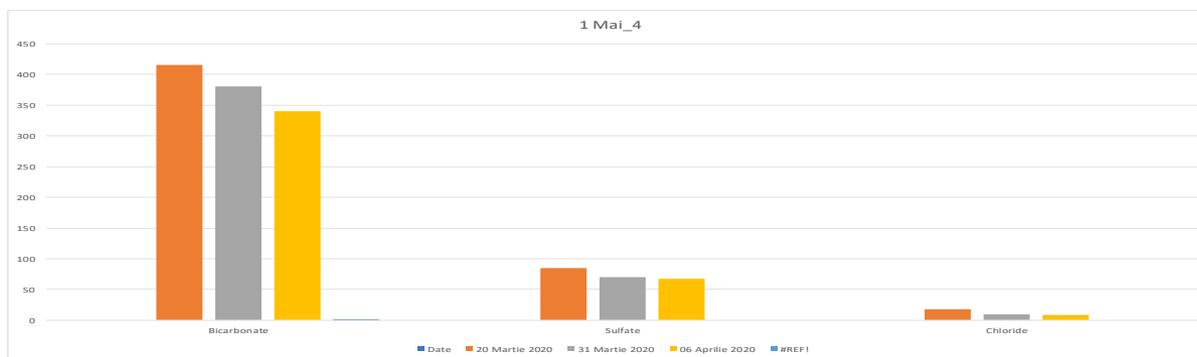
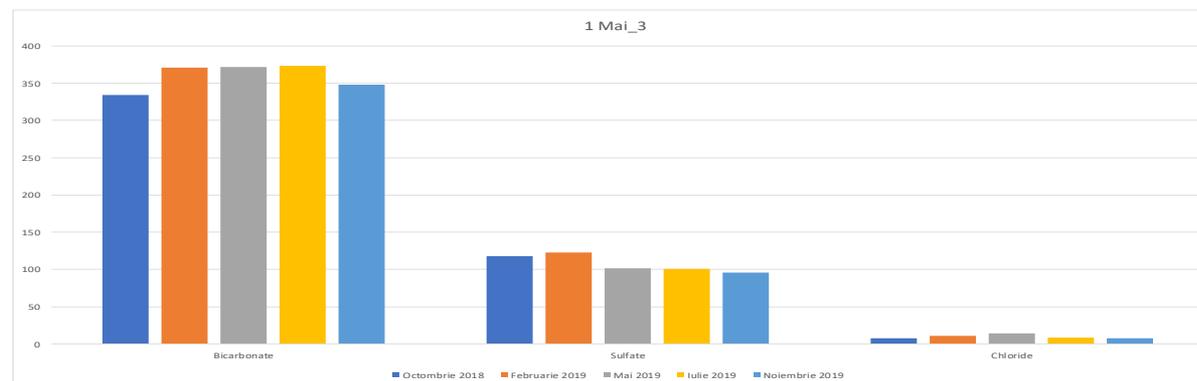
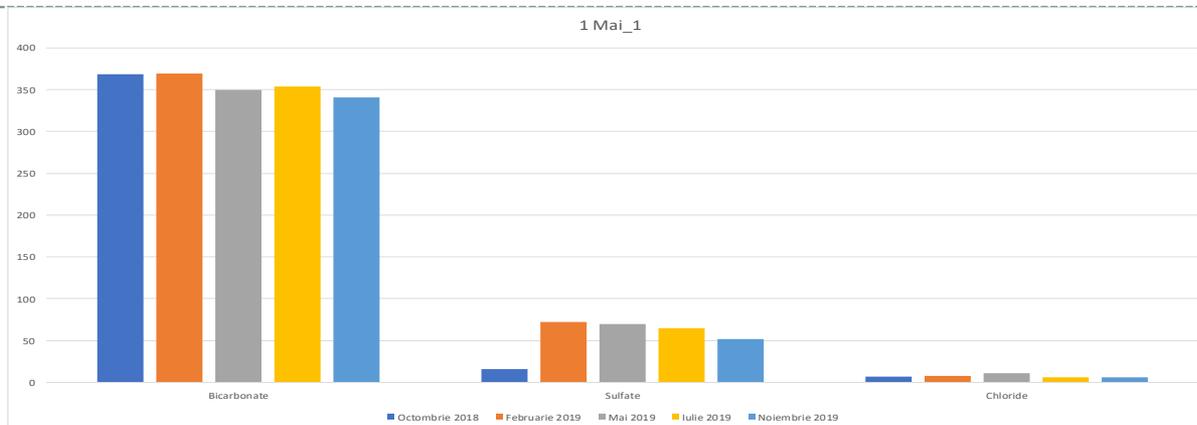
Taking into account the results obtained during the project implementation period, an assessment of the chemical characteristics of the waters from various locations could be done, comparatively, depending on the sampling campaign period, classified on different components criteria.

A grouping was performed on major anions, major cations and ions existing in extremely low concentrations, in traces, in the waters studied.



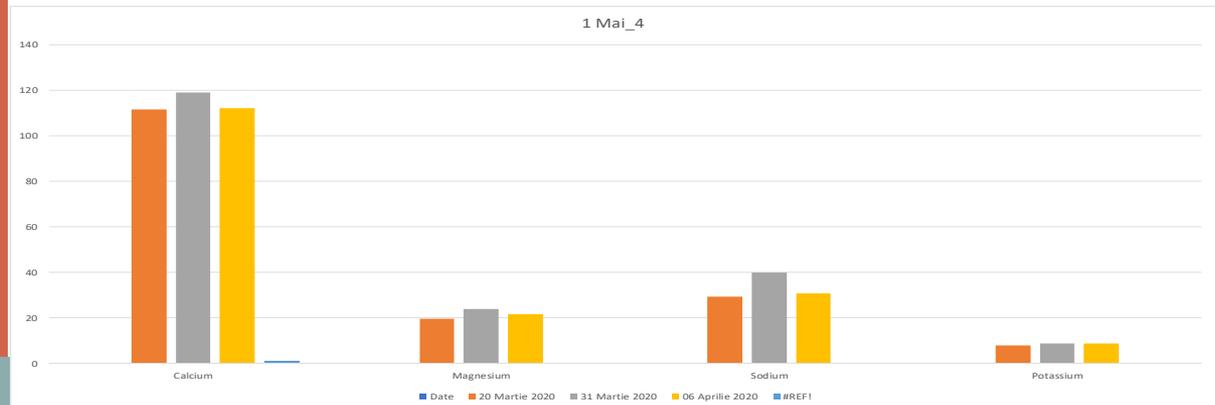
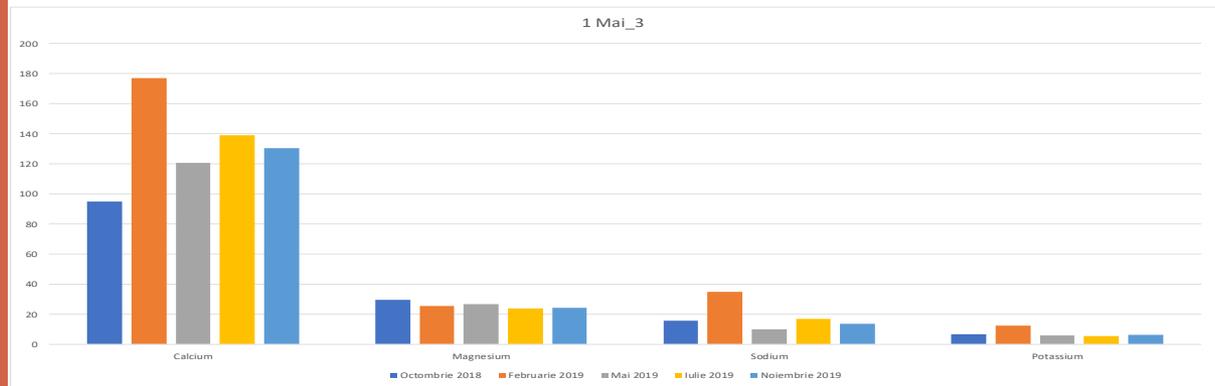
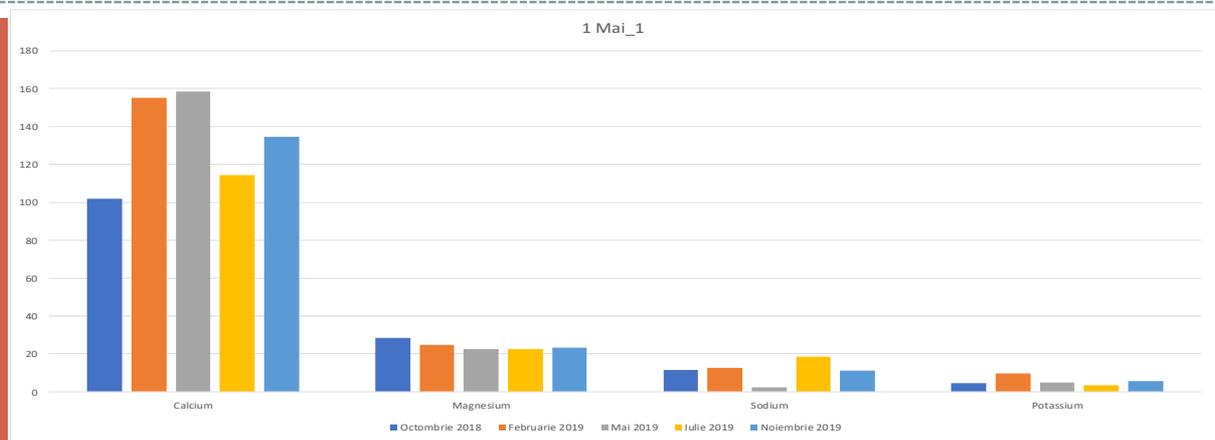
## RESULTS AND DISCUSSIONS

It could be noticed that with the regeneration of the Pârâul Pețea Natural Reserve from Băile 1 Mai, water samples were taken (1 Mai\_4) from "Ochiul Mare" and the results of the anion analyzes fallen within the concentration limits of other sources from Băile 1 Mai. Once the water level in the "Ochiul Mare" had been stabilized, the bicarbonate concentration was around 350 mg / l, as in the analyzed waters from the other sampling points from Băile 1 Mai.



## RESULTS AND DISCUSSIONS

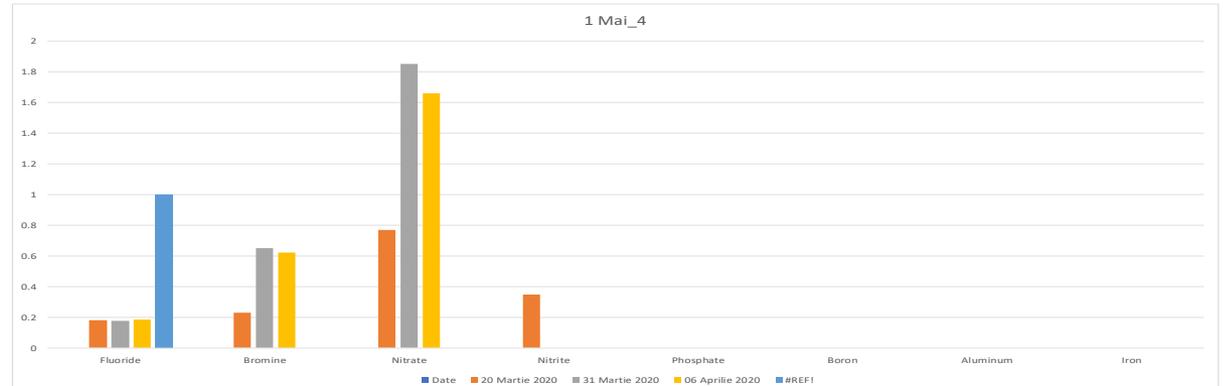
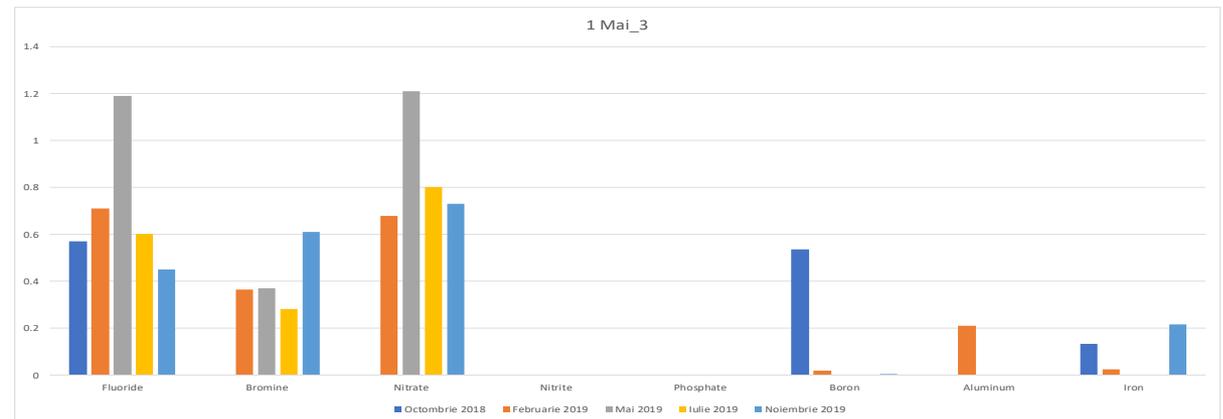
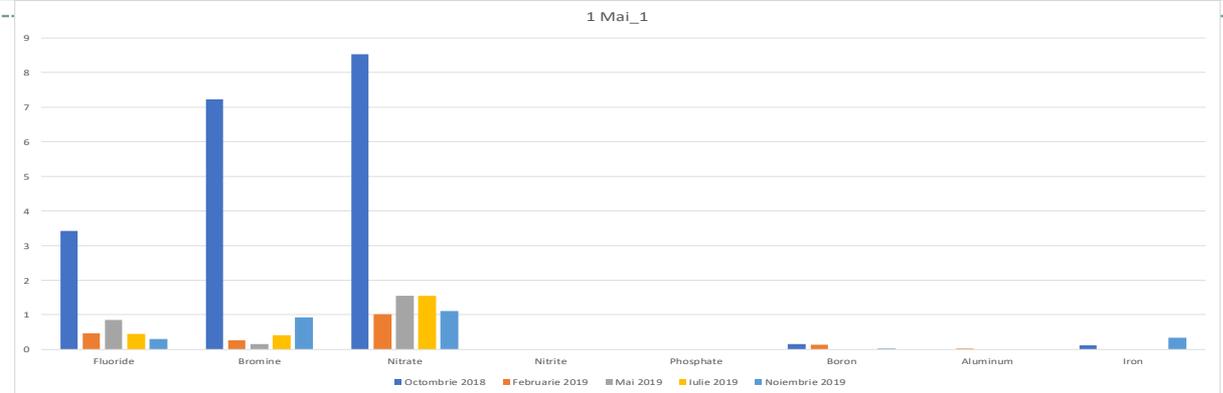
From the point of view of the major cations it results that the **calcium ions are dominant**, reaching in certain periods of the year concentrations of 160 mg / l. At 1 Mai\_4 the calcium concentrations was around 120 mg / l, as in the other sources from 1 Mai sampling points during the last determinations. The concentrations of magnesium and potassium ions in these waters were very similar, and the sodium concentrations registered variations, but in small limits, in the waters from 1 Mai.



## RESULTS AND DISCUSSIONS

Among the components present in traces, the presence of nitrates was constantly observed in all the analyzed samples.

*The evaluation of the results obtained regarding the composition in majority anions, majority cations and trace components for water taken from all selected sources in Oradea, Aleșd, Felix and 1 Mai was performed similarly, based on the results accumulated following sampling campaigns carried out during project development. The results were presented in detail in the research reports.*

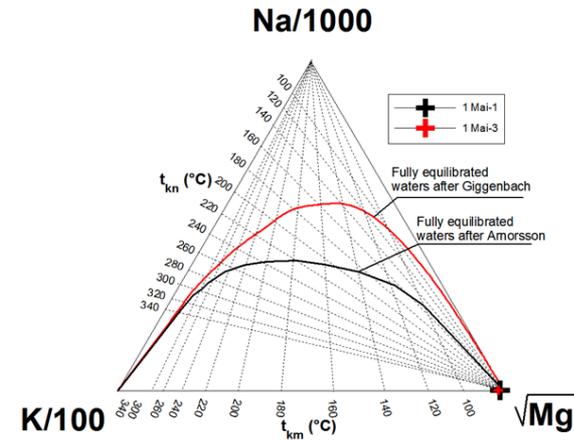
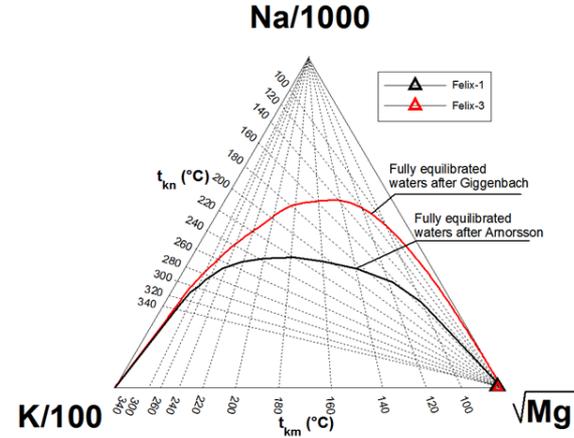


# RESULTS AND DISCUSSIONS

Taking into account the majority of cations, ternary Na-K-Mg diagrams were plotted (Giggenbach), (Arnorsson), from which conclusions are drawn on the established fluid-mineral equilibria.

The examples illustrated in the figures indicates that the studied waters are partially balanced, being close to the Arnorsson equilibrium curve. The partial equilibrium may be the consequence of the reactions of the fluid with the rocks it penetrates or it could be the result of the mixing with waters coming from feed zones of different temperatures.

## Equilibrium Diagrams

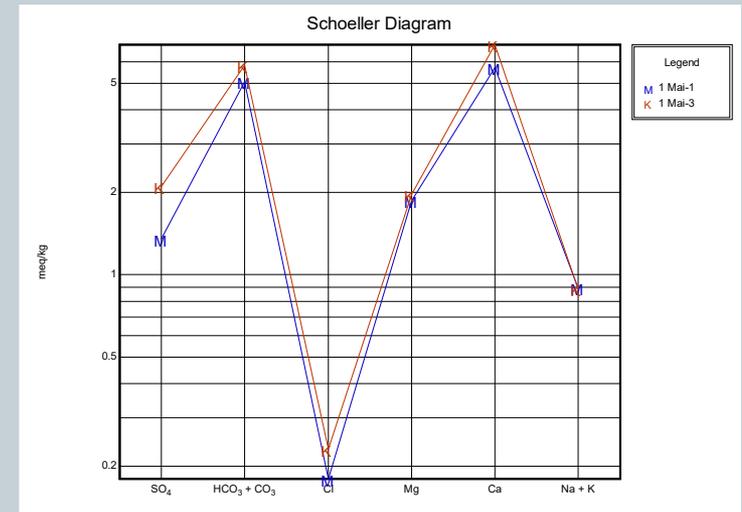
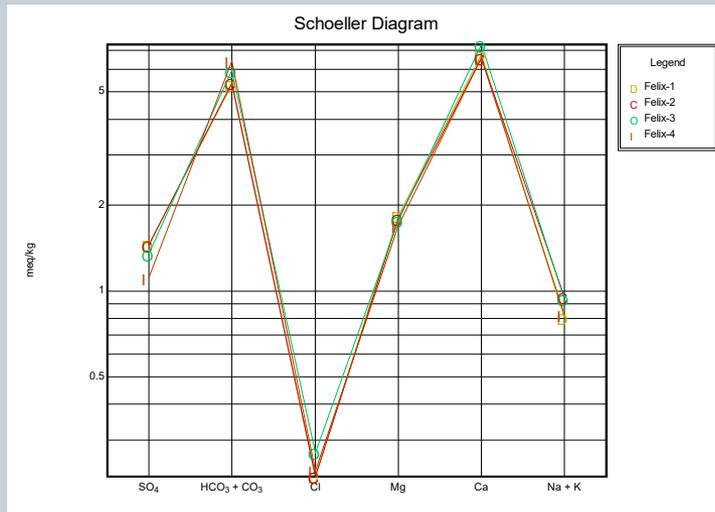


# RESULTS AND DISCUSSIONS

## Schoeller diagrams

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Gathering results of the analyzes of the main anions and cations in the studied waters, based on the Schoeller diagrams, it can be observed that the waters from Felix and those from 1 Mai have chemical compositions that fall into the same characteristics.

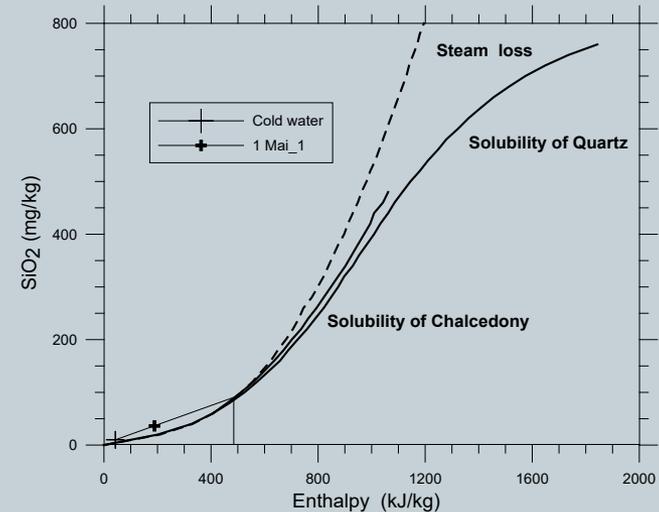
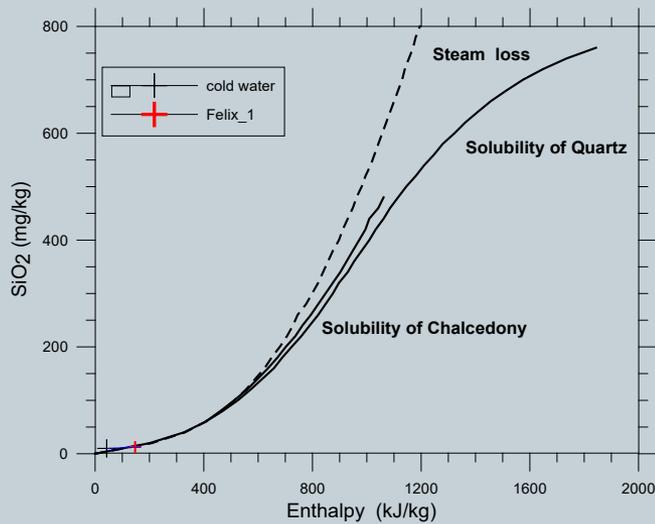


# RESULTS AND DISCUSSIONS

## Mixing models

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Another aspect was the estimation of the deep temperature assuming that the temperature of the geothermal water at the wellhead is the result of mixing on the way to the surface of hot deep water with colder water from shallow areas. Based on the spectrophotometrically determined silica concentration in the sampled waters and taking into account the water temperature measured at sampling, using a mathematical model, the depth water temperature in the geothermal reservoir was obtained.



Based on this model, can be concluded that Felix waters are shallow waters, the temperature of the hot component corresponding to the temperature measured at the surface. An example for one of the sources from Felix is shown . In case of the waters from 1 Mai, for the sample taken from the immediate vicinity of the “Ochiul Mare” results a deep water of high temperature, 115°C (fig. ), and for the other samples from 1 Mai the temperature of the hot source corresponds to the one measured at the surface .

## CONCLUSIONS

- From a chemical point of view, the studied waters in the Oradea - 1 Mai - Felix basin can be classified as following:
  - the waters from Felix and 1 Mai are *calcium-bicarbonated*,
  - the waters from the sources in Oradea are *calcium-sulphated*, having the tendency to pass to *calcium-bicarbonated-sulphate*, *calcium-sulphated-bicarbonate* and
  - *sodium-bicarbonated* in Aleşd; in Aleşd there is a resemblance to the anion composition of the waters of 1 Mai.
- The equipment used for the analyzes allowed also the detection of the constituents present in traces. The presence of *hydrogen sulfide* found in some waters, represents an increased risk of corrosion processes that may occur in the exploitation installations. The anions present in traces are: *fluoride*, *bromide*, *nitrate*, *nitrite*, *phosphate*. Boron concentrations in the studied waters are low, being below 1 g / l.
- The mineralization of the waters is higher for the waters from Oradea, having values of over 1 g / l, while for those from Felix and 1 Mai have values around 0.5 g / l. The pH of the waters varies from season to season for the same source.

# CONCLUSIONS

In the basin of the Petea brook is the Pârâul Petea Natural Reserve from Băile 1 Mai, in which the thermal lake with water lilies was located, clogged since 2012. **Fig.1** shows a picture taken on **16 February 2020**. The situation remained the same until the beginning of March 2020. Subsequently, following the restrictions imposed by the emergency situation triggered by the detection of COVID 19, the activity of geothermal water exploitation in the resorts Felix and 1 Mai in treatment bases and pools was stopped. Three days after the interruption of the production activities (**14.03.2020**), the appearance of water was found on the bottom of the basin of the Pârâul Petea Natural Reserve from Băile 1 Mai (**fig. 2**), in the conditions in which no rains were signaled. The water level in the natural basin gradually increased (**fig. 3**) (**20.03.2020**), until the end of March (**31.03.2020**) reaching the maximum level (**fig. 4**) existing ten years ago and probably known by many of us since childhood, in which the species Nymphaea Lotus var. Thermalis makes us happy with its existence in this reservation.

