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HYDROGEOCHEMICAL CHARACTERIZATION AND QUALITY OF GROUNDWATER IN THE SEBSEB REGION, GHARDAÏA PROVINCE (SOUTHERN ALGERIA)

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Abstract: *The study of the hydrogeochemical characteristics of the groundwater samples made it possible to assess the impact of this process on the degradation of the quality of borehole water in the province of Sebseb. Samples taken from 10 boreholes across the study region were analyzed for the determination of physicochemical characteristics such as pH, electrical conductivity, temperature, bicarbonates, chlorides, sulphates, nitrates, ammonium, calcium, magnesium, sodium, potassium and total dissolved solids (TDS).*

Examination of the variation in the hydrogeochemical composition of groundwater indicates high concentrations for all parameters (anions and cations) except potassium, sodium and electrical conductivity. The hydrogeochemical evolution of groundwater in Sebseb province was mainly controlled by the dissolution / precipitation of carbonate, sulphate and chloride minerals. The dissolution of minerals may explain the chemical characteristics of the waters studied.

The waters of the Sebseb region undergo deterioration in their quality and are no longer drinkable from a physicochemical point of view. The result of the saturation index calculation showed that most of the water samples were saturated or supersaturated with respect to carbonate minerals (calcite, dolomite and aragonite) and sulphate minerals (anhydrite and gypsum). Understanding the hydrogeochemical process can strengthen their protection for a sustainable use of these groundwater resources.

Keywords: *Hydrogeochemistry, physico-chemical quality of water, groundwater, Sebseb, South Algeria.*

1. Introduction

Water is a very important component of the earth's environment. Throughout human history, water has always supported life and served communities. However, the importance of the quality of the available water cannot be overestimated [1].

As a result, groundwater is not entirely pure as it generally contains mineral ions [1], [2]. The type and concentration of these dissolved minerals can affect the usefulness of groundwater for different purposes [3].

The geochemistry of groundwater is currently the subject of specific programs in many countries, particularly with a view to determining the geochemical background [4]. Often, the composition of water does not represent a state of equilibrium but a step along a succession of reactions leading to a state of global equilibrium [5]. Different waters collected in a given aquifer can represent stages of water-rock interaction along the same

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evolutionary process. In fact, the quality of groundwater is also deteriorating due to climate change resulting in low precipitation and high evapotranspiration [6].

The quality of groundwater in an area depends largely on natural processes, such as the dissolution and precipitation of minerals, the velocity of groundwater, the quality of recharge water, and the interaction with other types of aquifers. The alteration and erosion of hydrographic basins are anthropogenic inputs, in particular urbanization, agricultural and industrial activities [7-9].

Among the natural factors, the geology of the watershed, the degree of chemical alteration of the different types of rocks and inputs from sources other than the water-rock interaction play an important role in the control of water chemistry [10], [11]. Over the past decades, numerous studies have been published on the main ions, trace elements and potentially harmful elements in water, providing information on possible geological and anthropogenic influences on aquifers [12-14].

In the Sebseb region, a desert province, groundwater has been the only resource for human consumption and agricultural needs since very ancient times [15].

The main objective of this work is to provide information on the geochemistry of the waters of the region studied, to describe the variations in the concentration of major elements and some nutrients, to understand the mechanisms responsible for these variations in order to determine the physicochemical quality of these waters, considered as the only resource used in drinking water in the province of Sebseb.

2. Matherials and methods

2.1. Study area

The commune of Sebseb is part of the province of Ghardaïa; it is located 60 km from the main city and 663 km south of the capital Algiers. Its geographical position gives it an influence of the Saharan climate, arid and hot (Fig. 1). The M'Zab Chebka is made up of a multitude of small wadis born from the junction of several small ravines. The Sebseb valley is the widest among these wadis and is recognized for its groundwater potential.

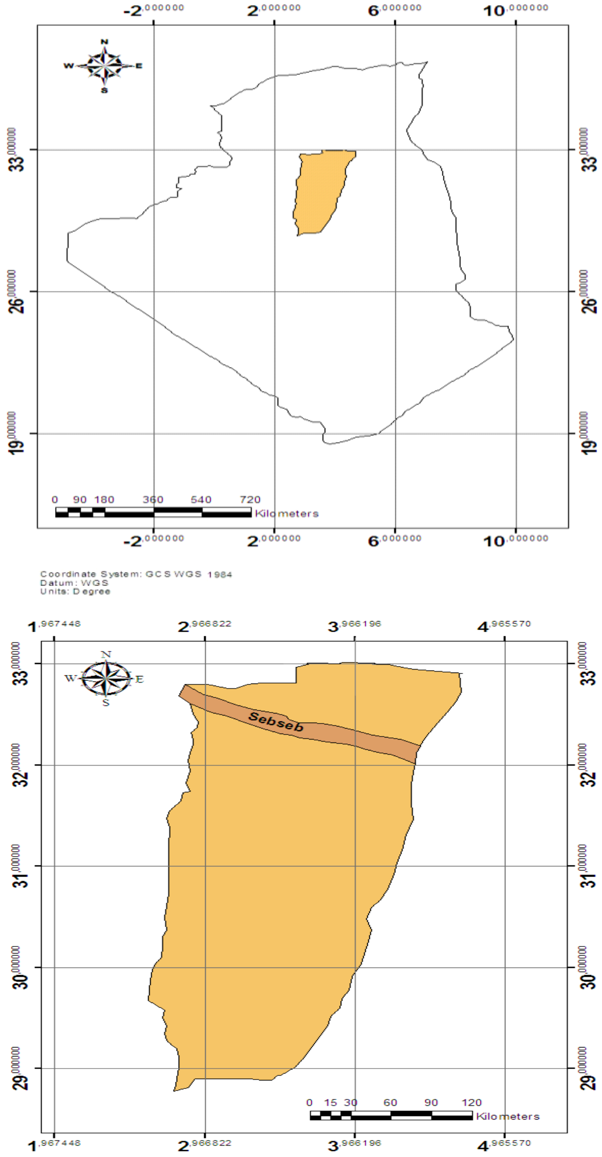

Fig. 1. Situation map of the study area

2.2. Geological overview

The geological synthesis of this region of southern Algeria shows that the Sebseb valley rests on a formation that belongs to the continental Quaternary. This structure is in the form of beds of wadis, depressions and dunes. It is located at the western edges of the secondary sedimentary basin of the Sahara, on a large subhorizontal plateau of limestone massifs of Turonian age. The thickness of these limestone massifs intersected by soundings is of the order of 110 meters. Under the Turonian limestones, we cut an impermeable layer of 220 meters formed of green clay and marl rich in gypsum and anhydrite. It is attributed to the Cenomanian. The Albian stage is represented by a large mass of fine sands, sandstone and green clays. It is home to considerable water resources, and its thickness is around 300 meters (Fig. 2).

Quaternary alluvium formed by sands, pebbles and clays line the bottom of the valleys of the wadis of the ridge, their thickness varies from 20 to 35 meters [16].

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2.3. Sample status and analysis data

Sampling was carried out on wells in the town of Sebseb (Fig. 3). The results of 10 samples analyzed during the observation period of September 2017 are reported in Table 1.

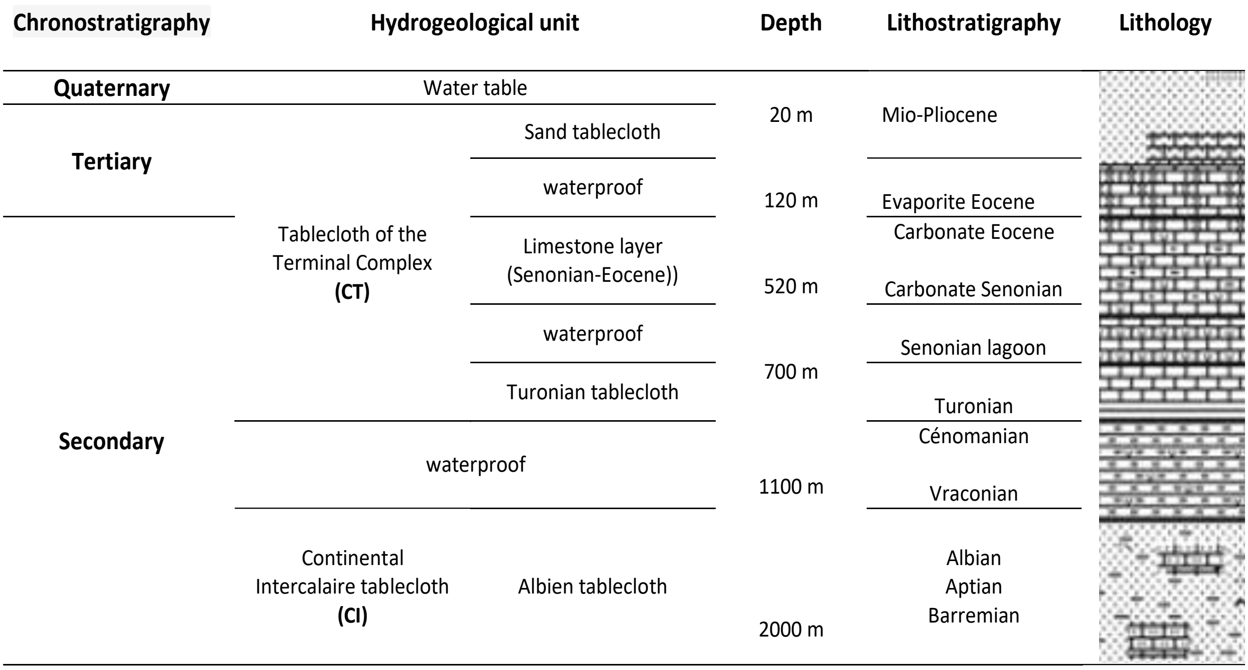

Fig. 2. Lithostratigraphic column from the Ghardaïa region (M'zab Valley)

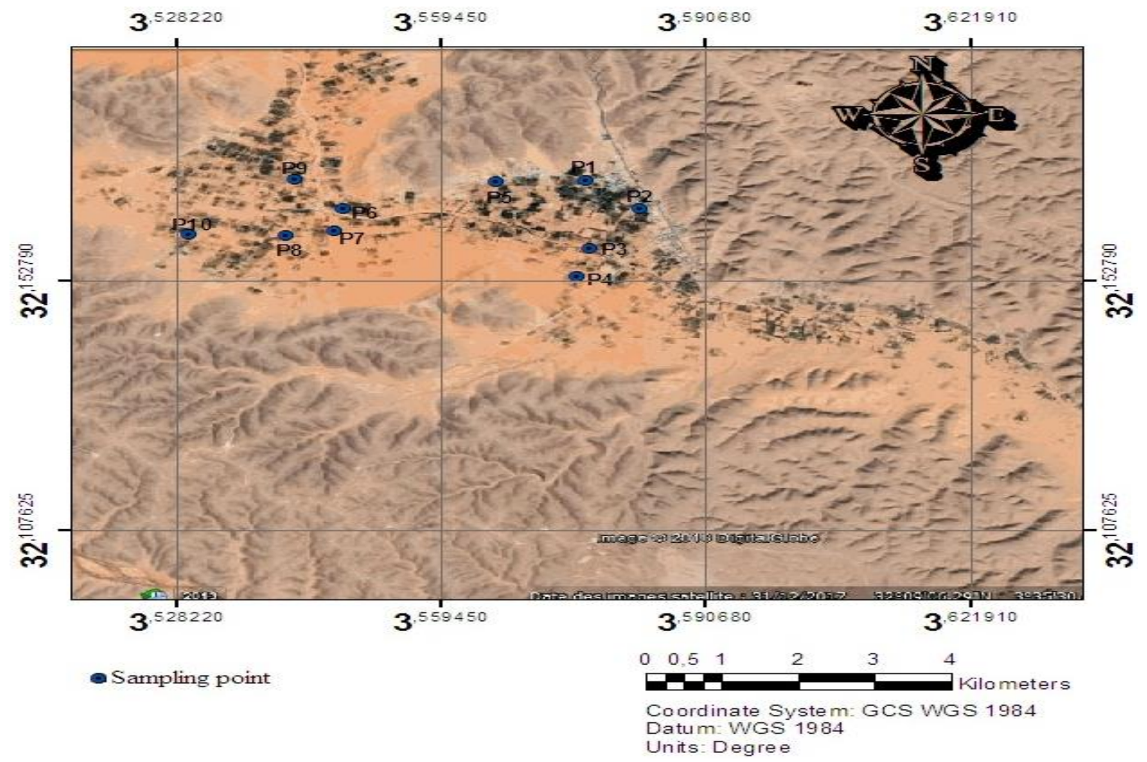

Fig. 3. Sampling point inventory map

Table 1

Data from analyses carried out in the region of Sebseb

Sampling points		P1	P2	P3	P4	P5	P6	P7	P8	P9	P10
Parameters											
T°C		22.60	22.50	22.40	22.10	22.60	16.20	18.20	21.10	17.50	16.90
pH		7.64	7.61	7.66	7.62	7.52	7.43	8.27	8.41	7.48	7.90
Cond. 25°C µS/cm		1514.00	1445.00	1520.00	1551.00	1487.00	1529.00	1480.00	1554.00	1465.00	1522.00
HCO_3^-	(mg/l)	156.16	200.08	148.40	161.04	139.08	143.96	287.92	305.00	139.08	278.16
Cl^-		273.70	251.01	260.93	268.02	249.59	276.53	266.61	226.90	255.26	218.39
SO_4^-		654.76	670.83	629.26	522.67	590.16	535.02	416.90	461.76	535.02	449.43
Ca^{++}		190.78	181.16	192.38	184.37	185.97	139.47	134.67	153.91	107.41	157.11
Mg^{++}		95.26	79.70	81.65	89.42	86.51	32.07	88.45	71.93	46.65	77.76
Na^+		183.33	155.56	166.67	161.11	194.28	167.00	163.63	180.00	162.00	168.18
K^+		9.00	10.00	10.00	17.00	7.50	6.20	10.00	8.75	10.00	6.25
NO_3^-		14.81	14.54	15.38	8.37	11.55	12.14	10.25	17.52	10.28	12.12
NH_4^+		0.02	0.02	0.02	0.02	0.01	0.01	0.01	0.01	0.00	0.26
TDS		880.00	840.00	880.00	904.00	864.00	904.00	858.00	901.00	866.00	882.00

3. Results and discussion

3.1. Chemical facies

Given the predominance of ions (Na^+, Cl^-, Ca^{++} and SO_4^{--}) in the water of the aquifer sampled, a representation of the chemical facies in the Na^+/Ca^{++} and Cl^-/SO_4^{--} diagram (Fig. 4), shows the existence of two characteristic poles of the water table considered. These two poles are represented by the sulphate-sodium facies and the other, sulphate-calcium.

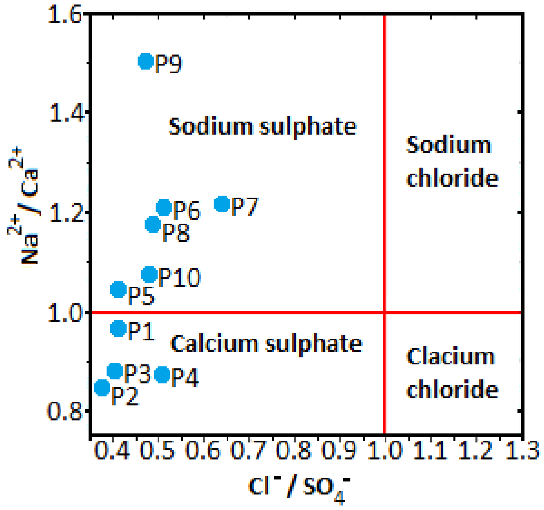

Fig. 4. Geochemical facies of surface waters (Reports: (Na^+/Ca^{++} - Cl^-/SO_4^{--})

3.2. Saturation index

The saturation index is calculated by the Debye-Huckel law (1923):

$$IS = [\log (Q)] / [\log (Kps)]$$

of minerals dissolved in water (Table 2). The steady state of this index is in the range of -0.5 to +0.5.

Chloride (Cl^-) ion only precipitates at higher ionic strengths, so it is a good indicator of the state of concentration of water.

The order of the elements classified by molality is not always the same because the elements do not concentrate in proportion to the concentration factor. The contents of some elements increase while others decrease [18].

3.3. Concentration diagram

The results of analyzes are represented in concentration diagrams with the logarithm of the molalities ($meq.l^{-1}$) on the ordinate and the logarithm of the concentration factor on the abscissa.

Table 2

Variation in saturation indices of some minerals and CO_2 partial pressure

Sample	Aragonite	Calcite	Dolomite	Anhydrite	Gypsum	Halite	Sylvite	CO_2	NH_3	O_2	Log PCO_2
P1	2.64	2.79	5.34	1.19	1.50	-3.35	-4.07	-0.96	-8.76	-37.47	-2.52622
P2	2.69	2.83	5.36	1.17	1.48	-3.47	-4.08	-0.81	-8.78	-37.62	-2.38902
P3	2.65	2.80	5.28	1.19	1.50	-3.41	-4.04	-1.00	-8.72	-37.45	-2.56591
P4	2.65	2.80	5.34	1.12	1.43	-3.40	-3.77	-0.93	-8.75	-37.72	-2.49377
P5	2.49	2.63	5.00	1.16	1.47	-3.35	-4.18	-0.89	-9.05	-37.95	-2.46042
P6	2.24	2.39	4.14	0.99	1.37	-3.37	-4.14	-0.77	-9.45	-40.56	-2.39469
P7	3.30	3.45	6.75	0.85	1.22	-3.38	-3.93	-1.38	-8.55	-36.48	-2.89894
P8	3.49	3.64	7.02	0.94	1.27	-3.43	-4.11	-1.51	-8.43	-34.90	-2.99827
P9	2.17	2.32	4.30	0.89	1.26	-3.42	-3.98	-0.82	-3.42	-39.89	-2.44733
P10	3.01	3.16	6.02	0.95	1.32	-3.46	-4.21	-0.99	-7.58	-38.42	-2.55658

The water concentration factor (FC) can be estimated from the ratio between the Cl^- content of a water and the minimum value of the Cl- content from the database. This allows a relative classification of the samples with respect to each other [17].

3.3.1. Concentration diagram of the major elements

The sulphated facies is dominant in the groundwater collected at Sebseb. The high concentration of SO_4^- is possibly due to the dissolution of anhydrite and gypsum which are marked by a supersaturated saturation index (Fig. 5). These two minerals can come from the dissolution of marl rich in gypsum and anhydrite.

The HCO_3^- bicarbonate content decreases faster than the concentration factor. This is due to the precipitation of carbonate minerals. The concentration of carbonate alkalinity in the waters of the region may be due to the dissolution of limestones present in the study area.

The evolution of the CO_3^- ion is mainly due to the presence of the latter in the compounds of aragonite $CaCO_3$, Calcite $CaCO_3$ and dolomite CaMg $(CO_3)_2$ which are marked by a supersaturated saturation index (Table 2).

The evolution of Na^{+2} starts from the log (Fc) close to 0 up to 0.06. After that, the sodium molalities are decreasing to the value log (Fc) = 0.07. Then, it increases a second time from the log (Fc) and becomes greater than 0.07. The strong sodium molalities can be explained by a simultaneous dissolution of chlorides and sodium from the same origin; we are talking about Halite which is under-saturated.

Magnesium Mg^{+2} and calcium Ca^{+2} are marked by weak molalities; their evolution with the concentration factor seems to be identical. This can be explained by the common origin of the latter two; we are talking here about the dissolution of dolomite CaMg $(CO_3)_2$, the mineral is marked by the greatest saturation index.

When the water concentrates, the calcium contents increase, the alkalinity (Alc) increases and then decreases according to the law of residual alkalinity. As long as the waters are undersaturated with respect to calcite, Ca^{+2} and Alc can increase simultaneously. When equilibrium with this mineral is reached, the Ca^{+2} content increases and the alkalinity decreases because Ca^{+2} > Alc, residual alkalinity: positive calcite [19].

Potassium shows very low concentrations. However, a significant increase is noted in some samples (participation in probable Sylvite precipitation (KCl) then a contribution of this element which increases its concentration), and a decrease for other samples. But in general, the evolution of potassium remains very slow than the concentration factor [20].

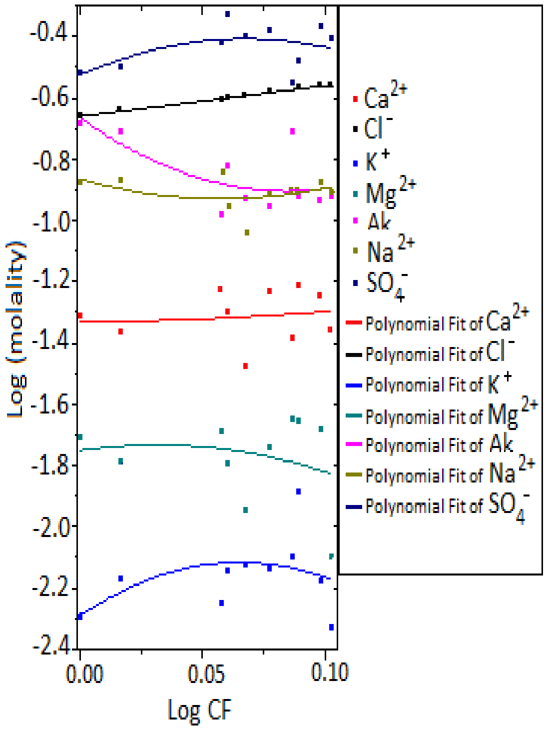

Fig. 5. Concentration diagram of major elements

3.3.2. Nutrient concentration diagram

For NO_3^- nitrates, there is a stabilisation in the evolution of the latter with the concentration factor (Fig. 6). The NH_4^+ ammonium content decreases slightly with respect to the concentration factor. This can be explained by the transformation of ammonium into nitrite and then into nitrate. In an oxidizing medium, ammonium is transformed into nitrites and then nitrates, which induces oxygen consumption [21]. The presence of ammonium in water is believed to be related to the denitrification process by oxygen consumption and its concentration increases when the water contains a low O_2 content and a high CO_2 content.

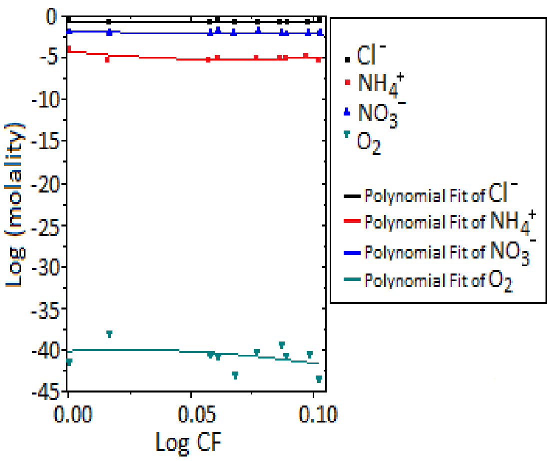

Fig. 6. Nutrient Concentration Diagram

3.3.3. Carbonate concentration diagram

Carbon dioxide CO_2 is marked by a perfect evolution with the concentration factor. This evolution may depend on a chemical reaction between calcium and bicarbonates, which induces the composition of calcite and the release of carbon dioxide (Fig. 7).

Alkalinity is conservative in the sense that it is not affected by the gain or loss of CO_2, the dissolution or precipitation of a strong acid or strong base salt [22], [23]. However, it can be modified by the precipitation or dissolution of weak acid or base salts.

Saturation indices of the main carbonate minerals (calcite, dolomite and aragonite) show that they are in equilibrium. This state of carbonate minerals indicates that the water has undergone significant changes as a result of CO_2 degassing. This induces precipitation of some of the carbonate minerals [24].

In natural solutions, interactions with minerals are the main controls on Alc and calcium, with calcite being the first mineral involved [25]. The calco-carbonic equilibrium reaction can be written:

$$CaCO_3(s) + CO_2(g) + H_2O \leftrightarrow Ca^{+2} + 2HCO_3^-$$

The HCO_3^- bicarbonate content decreases faster than the concentration factor. This may be due to collusion with calcium to give calcite as shown in the previous equation or the dissolution of bicarbonates which gives carbonate ions CO_3^{-2} and hydrogen ions, explained by the following equation:

$$HCO_3^- \leftrightarrow H^{++} CO_3^{-2}$$

The decrease in molalities of the CO_3^- ion and mainly due to the collusion of the latter with calcium to give calcite:

$$Ca^{+2} + CO_3^{-2} \leftrightarrow CaCO_3$$

The reaction can also combine a hydrogen ion to give HCO_3^- bicarbonates.

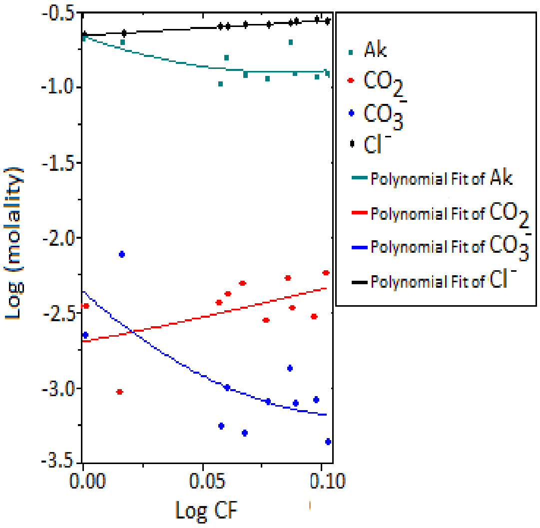

Fig. 7. Carbonates concentration diagram

3.3.4. Water-calcite balance diagram

We plot the log line:

$(Ca^{2+}) + 2pH + \log(H_20) + \log(pC0_2) = 9.76$

Over-saturation increases when estimated pCO_2 decreases (Fig. 8) a phenomenon that has been already observed in literature [26-29]. Sebseb's groundwater is therefore supersaturated with respect to calcite (Fig. 8).

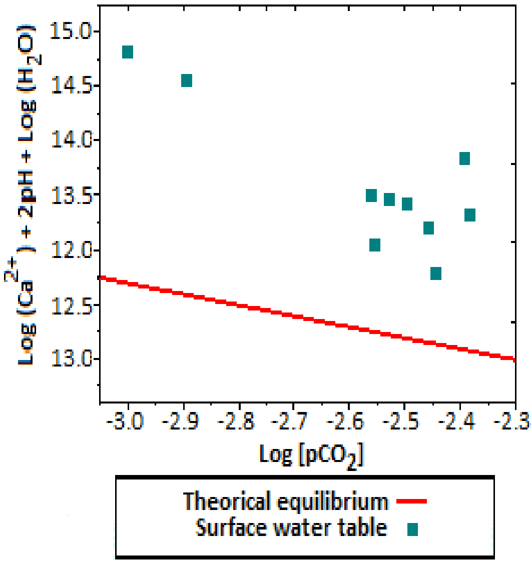

Fig. 8. Water-calcite balance diagram

3.3.5. Water-dolomite balance diagram

In the same way as for calcite, by plotting the log line $(Ca^{2+}) + \log(Mg^{2+}) + 4pH$ as a function of $2.\log(pCO_2)$. With log:

$(Ca^{2+}) + \log(Mg^{2+}) + 4pH = 19.2 - 2.\log(pCO_2)$

The remarks are generally the same for saturation with respect to calcite and dolomite. All samples are in a state of over-saturation (Fig. 9).

It can be concluded that saturation with carbonates (calcite and dolomite) is a factor in controlling water mineralization. In this case, saturation is the limiting factor.

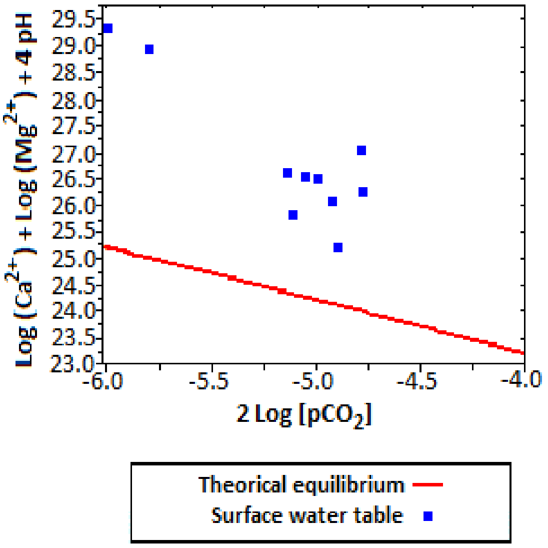

Fig. 9. Water-dolomite balance chart

3.3.6. Mineral stability index according to Ph

The saturation indices of carbonates (Calcite, dolomite and aragonite) increase steadily with pH, but this is not the case for sulphates, which remain almost stable and no longer increase with pH (Fig. 10a). The alkalinity produced by the dissolution of carbonates is the main cause of the increase in pH [20].

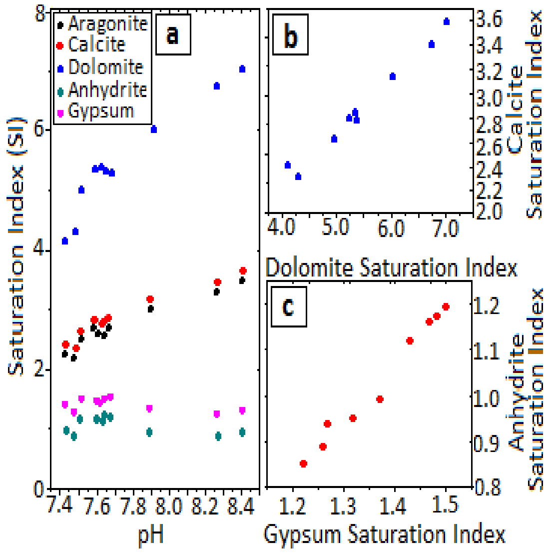

Fig. 10. Variation in the stability index minerals by Ph

The SI of carbonate and sulphate minerals follows a positive linear trend, which suggests that the mineral phases are changing with a similar trend following the same hydrogeochemical process (Figs. 10b, 10c).

3.3.7. Log (pCO_2) and IS relationship of minerals

The Log (pCO_2) vs IS bonds of carbonates (Calcite, dolomite and aragonite) show that all the samples are in equilibrium (supersaturated) and tend to precipitate (Fig. 11). Sulphates (Anhydrite and Gypsum) are also in a state of equilibrium and can precipitate.

On the other hand, the Log bonds (pCO_2) with the main chlorinated minerals (Halite and Stylites) show that these waters are under saturated, which induces dissolution of these minerals.

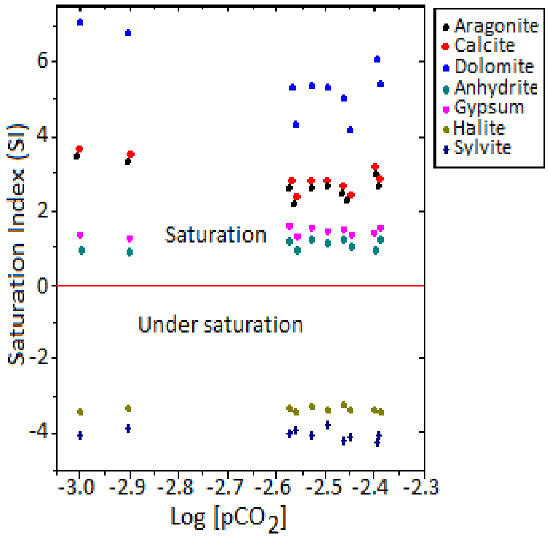

Fig. 11. Relation Log (pCO_2) - minerals SI

3.4. Physico-chemical water quality

The purpose of the physico-chemical analysis is to demonstrate that the wells studied have concentrations that meet drinking water standards or not. The results were compared with the values prescribed in water quality standards in World Health Organization (WHO, 2017).

3.4.1. Physical parameters

The pH depends on the origin of the water, the geological nature of the substrate and the watershed crossed [30]. In the case of the study region, the pH values of the groundwater do not show significant variations, they all comply with the potability standard (Tab. 3). The temperature and the total dissolved solids (TDS) also show values which remain acceptable in terms of drinking water standards.

Table 3

Water Potability Standards (2017)

Parameters	**WHO standards**	**Parameters**	**WHO standards**
pH	≥ 6,5 et ≤ 9	K^+ (mg/l)	12
CE (µS/m)	1000	HCO_3^- (mg/l)	/
TDS (mg/l)	< 600	Cl^- (mg/l)	250
Ca^{+2} (mg/l)	200	SO_4^- (mg/l)	500
Mg^{+2} (mg/l)	150	NO_3^- (mg/l)	50
Na^{+2} (mg/l)	200	NH_4^+ (mg/l)	0.2

Therefore, electrical conductivity provides information on the degree of mineralization of water. The waters of the controlled points are mineralized (Fig. 12), with values that oscillated between 1445 and 1554 µS / cm. These high values seem to result from the leaching of the reservoir rock in which the water resides. These waters, compared to WHO standards for drinkability with respect to conductivity, are considered drinkable.

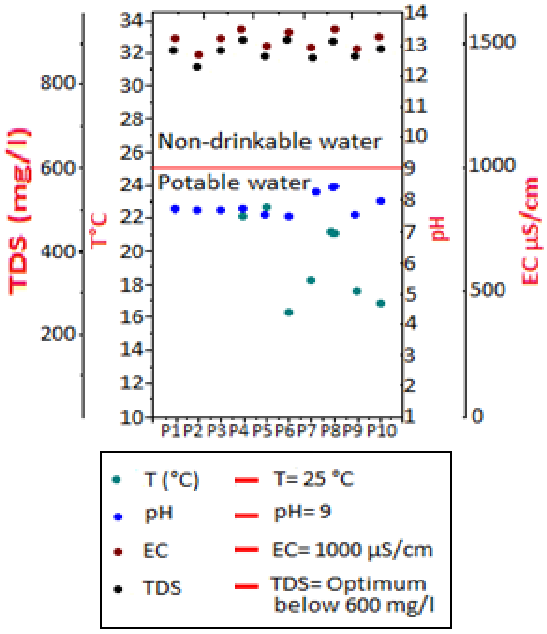

Fig. 12. Water quality in relation to physical parameters

3.4.2. Cations

Calcium is generally the dominant element in drinking water and its content varies mainly according to the nature of the terrain crossed, such as limestone or gypsum facies [31].

The high calcium contents could be attributed to the dissolution of sulphated and carbonated minerals, which are supersaturated in the waters of the region, which induces a non drinkability of these waters with respect to calcium. Magnesium Mg^{2+} comes from carbonic acid attack of magnesium rocks and the dissolution of magnesium in the form of carbonates and bicarbonates [32].

It is marked by concentrations above the drinking water standards with the exception of the P6 and P9 wells, which remain in compliance with the drinking water standards with respect to Mg^{2+}. In unpolluted groundwater without contact with evaporite, the sodium content Na^{2+} is between 1 and 20 mg / l [33].

The formations in the region are rich in evaporite, which explains the high sodium values despite the fact that these waters remain in compliance with admissible standards for drinking water. Potassium is generally the least abundant major element in water (Fig. 13).

The water of the region has a potability vis-à-vis this element. Potassium, in our case comes from the dissolution of Sylvite (KCl).

3.4.3. Anions

Sulphates (SO_4^-) show values greater than the guide value (500 mg / l) of the standard relating to the quality of water intended for drinking water supply, with the exception of three wells, which is the case of wells P7, P8 and P10. The very high presence of sulphates is due to the richness of the geological formations of the region in gypsum (Fig. 14).

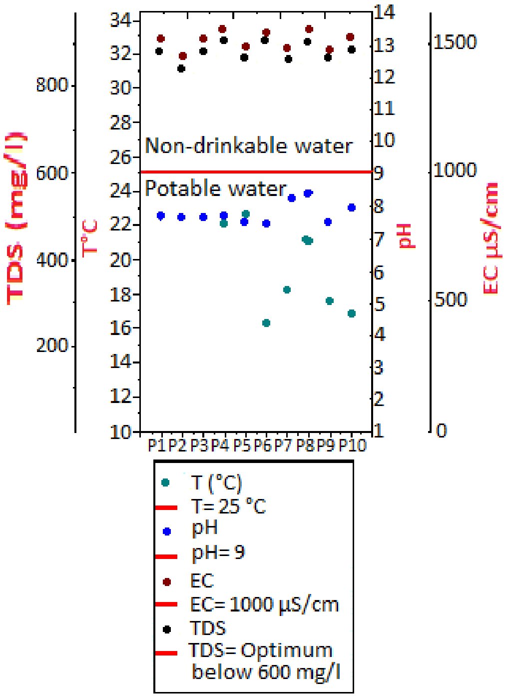

Fig. 13. Water quality with respect to cations

Water too rich in chlorides is laxative and corrosive; the concentration of chlorides in the water also depends on the terrain crossed [34].

Based on the results of analyzes carried out on the water samples, the chloride contents greatly exceed the standards for drinking water; they mainly result from the dissolution of Halite and Sylvites. The bicarbonate content in groundwater depends mainly on the presence of carbonate minerals in the soil and aquifer, as well as the CO_2 content of the air and soil in the catchment area [33].

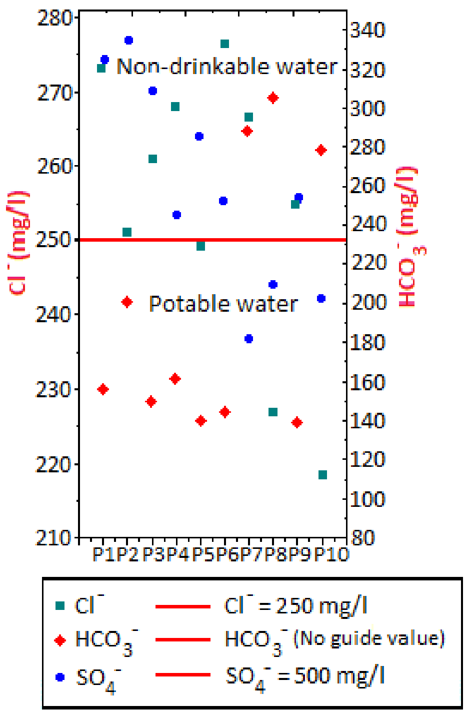

Fig. 14. Water quality with respect to anions

In the water analyzed, concentrations above the drinking water standards are observed for the P7, P8 and P10 wells and the other wells comply with the drinking water standards. The high values are probably due to the circulation of these waters in the aquifer reservoir through the limestone formations which characterize the region.

3.4.4. Nutrients

Nitrates are present in water by leaching nitrogenous products from the soil, by decomposing organic matter or synthetic or natural fertilizers [35].

Ammonium NH_4^+ is the most toxic form of nitrogen and the presence of ammoniums in large quantities is indicative of contamination by releases of human or industrial origin [20].

Nitrates and ammonium are low concentrations and are good for human consumption. In addition to these two elements, except the P10 well is marked by an ammonium concentration higher than the drinking standards, this is probably due to the use of chemical fertilizers in agriculture in the vicinity of this well (Fig. 15).

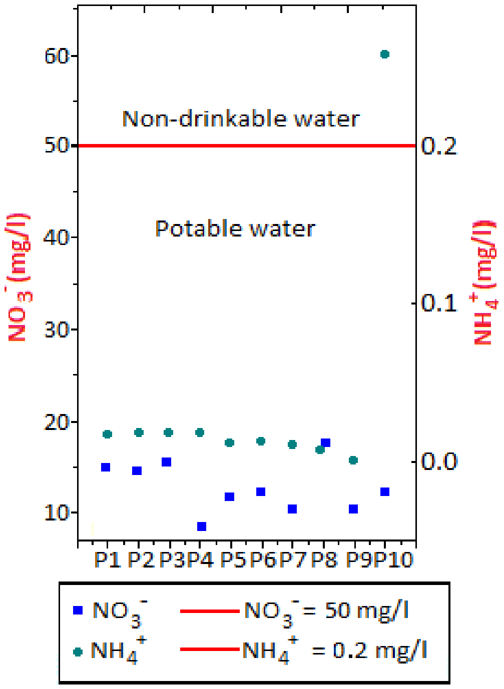

Fig. 15. Water quality with respect to nutrients

4. Conclusion

Groundwater is an essential water resource for drinking water supply in the Sebseb region. In this study, the saturation index was used to assess the hydrogeochemical evolution of groundwater in this area. Chemical analysis showed that Na^{2+}, Ca^{2+}, Cl^- and SO_4^{2-} were the dominant ions in all groundwater samples.

The results of the calculations of this index showed that most of the groundwater samples were saturated or supersaturated with regard to carbonate minerals (Calcite, Dolomite and Aragonite) and sulphate minerals (Anhydrite and Gypsum). All groundwater samples were undersaturated for chlorinated minerals (Halite and Sylvite).

The hydrogeochemical analysis of the groundwater in the study area was mainly marked by the alteration of rocks, which is to say by the dissolution of carbonate and sulphated and even chlorinated minerals. The dissolution of these minerals increases the concentration of chemical elements and almost all become higher than the standards of drinkability requiring treatment and demineralization of these waters before consumption.

5. Acknowledgments

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