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Hydro-geochemical Characterization of Water Springs of the Aurès region. (North-eastern Algeria)

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Abstract

The origin of the salinity of the Cretaceous and Pliocene-Quaternary aquifers of the Aurès region presents a challenge for the exploitation and mobilization of groundwater resources. In this region; people can estimate the quality of groundwater, via samples taken in wells, boreholes and in the springs. Evaporation, endorheic basin nature, population growth and expansion of irrigated areas are natural and anthropogenic stresses that can lead to salinization of water bodies. A multidisciplinary approach integrating hydrogeology, hydrochemistry and multivariate statistical analysis was undertaken to characterize and control the mechanisms of water mineralization. The main natural geochemical processes involved in the acquisition of the salinization are related to the interactions between the rocks and the water (dissolution of evaporite minerals), the cation exchange and evaporation.

Keywords: Aurès, salinity, salinization, evaporites, chemical tracers.

1. Introduction

The Aurès region is the eastern extension of the Saharan Atlas. It extends between parallels 34 ° - 45 ° and 35 ° - 30 North and longitudes 5 ° - 45 'and 7' 'to the east of the international meridian. The northern slope of the Aurès region is rich by a wealth of water springs of hot and cold deposits. The thermal springs emerge in the land of the Albo- Aptian of the Cretaceous consisting mainly of limestone and dolomitic limestone of the Cenomanian with gypsum inclusions, the whole is surmounted by covered red clay of Quaternary. These limestones are crossed by cracks and broken loopholes that allow infiltration and reassembled of the groundwater. [1, 5, 6].

The main objective of this study is the hydrogeochemical characterization of cold and thermal springs of Cretaceous and Quaternary Plio- aquifers of Aurès region; and the identification of the origin of the salinity by hydrogeochemical approach.

2. Experimental

2.1 study area

The study area is located on the north side of the massif of the Aurès, 13 water springs are located in Cretaceous and Pliocene-Quaternary aquifers. They were the subject of monitoring physicochemical measurements. (Fig.1). the climate of the study area is semi-arid, the average annual rainfall is 470 mm and the average annual temperature is around 16 ° C.

The northern slope of the Aurès has a simple structure: the anticline Chelia, 2328m (Ras Kaltoum) gradually occupied the southwest to the northeast by the geological formations of the Albo-Aptian. They are consisted by limestone, sandstone and dolomites. Jebel Bezaz developed mainly in the Aptian with two facies in the southwest (Jebel Feraoun 2093m) limestone, sometimes dolomitised, overcome alternations of marl and limestone, north (Ras Serdoun, 1700m), here; the facies is heterogeneous limestone. The Aurès syncline is characterized by outcrops of Cenomanian marls [1, 2, 5, 6]. On the edge of the Anticline Khenchela (Jebel Aidel) there Albian overlooking the thermal springs, it presents a sandstone facies at the top and bottom of dolomitic limestone and calcareous marl, it gets really deep marl. [1]. (Fig.2), (Fig.3).

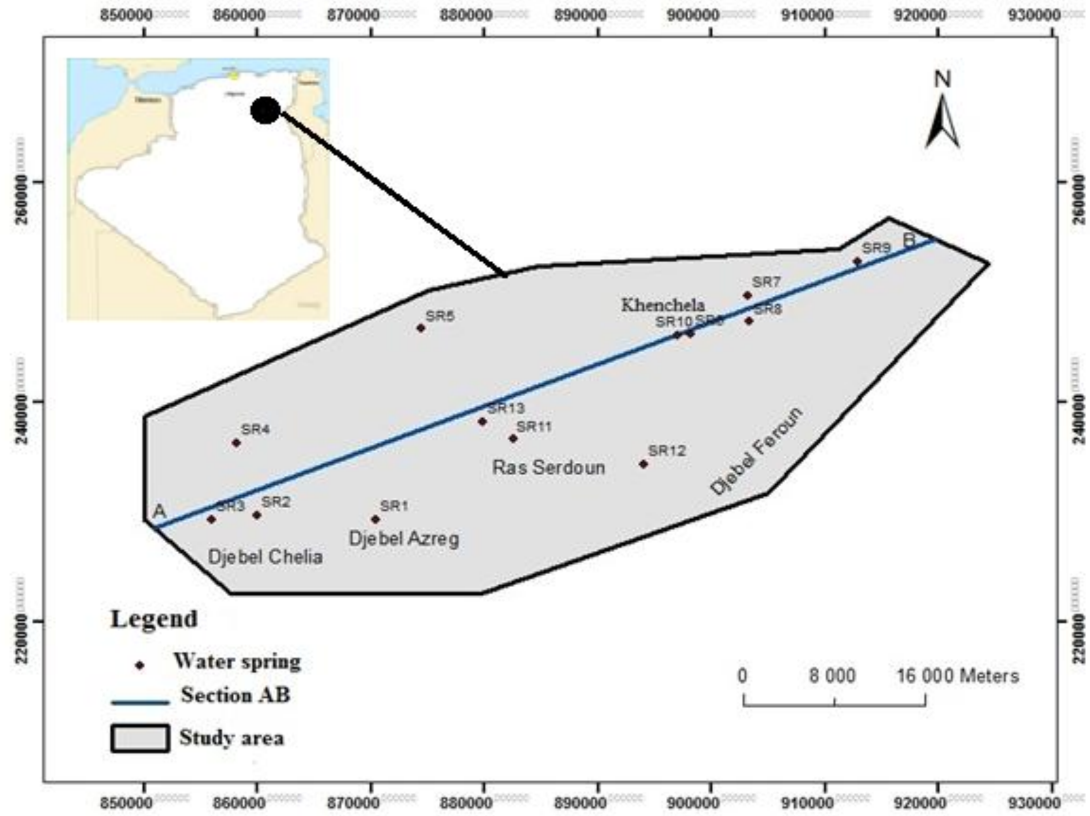

Figure 01: Location map of the study area. (May-2014)

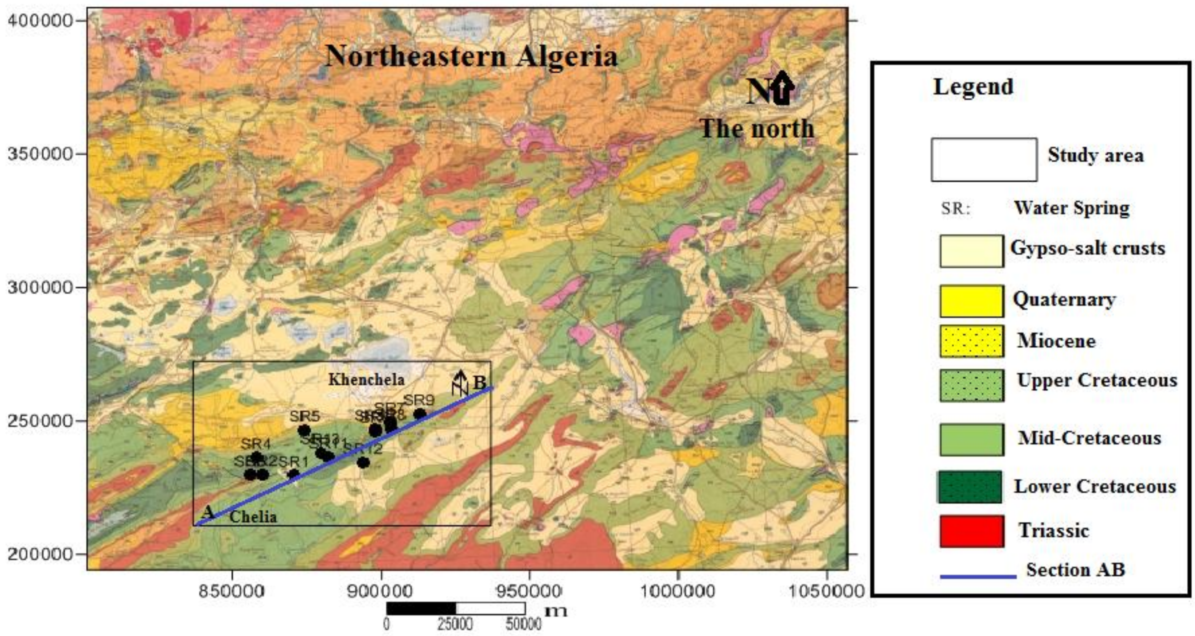

Figure 2: Geological map of study area. (May-2014**).**

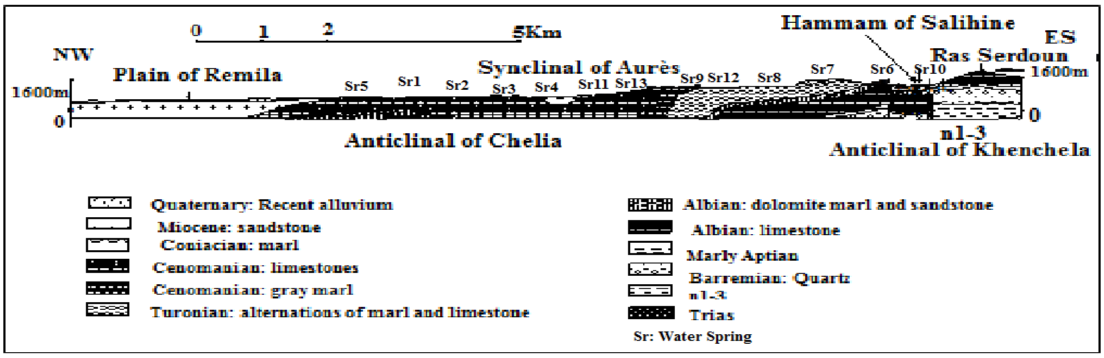

Figure 3: Interpretative Cup in northern massif of the Aurès region. **Modified [1].**

2.2. Sampling and Analytical Techniques

The analysis of water was made in May 2014. The measurement of the non-conserved physical parameters such as pH, temperature, electrical conductivity and mineralization was performed *in situ* using a Portable multi parameter type "Consort C931, version 2.4."

The major chemical elements were analyzed by ion chromatography phase. LACILAP laboratory (Ain M'lila. Algeria. May-2014).

We took the geological coordinates with a GPS type of Garming and measured four physical parameters in situ, seven major chemical elements and we calculated four saturation index.

The chemical facies is determined by software DIAGRAMME of the University of Avignon (France).

Calculating the saturation index (SI) was effected, with the software PHREEQC (USGS).

3. Results and Discussion

3.1. Physical parameters

Water temperature plays a crucial role in solubility of gases and salts. It is strongly influenced by environmental conditions related to the situation geographic the resort, geology traversed terrain, hydrology ecosystem and especially climate prevailing. [21].

The temperature of the cold springs varies from 13 to 17 ° C, with an average of 15 ° C; it is close to the average annual temperature. These are all water withdrawn high in the mountains. It seems that the catchment springs that have very low temperature are located at much higher altitudes than the points of emergence. The temperature of the thermal springs is much greater than the average annual temperature; it ranges from 33 ° C to 65 ° C, with an average of 49 ° C. It seems that these waters come from a very deep origin. They are influenced by the geothermal gradient in the region which is 4.19 ° C / 100 m and seismic activity. [1].

The pH depends on the natural conditions, such as vegetation cover and the nature of the soil substrate rocks and human activities [21]. It measured on the waters of the carbonate aquifer present values ranging from 6.42 to 7.00. The few values below 7 could correspond to the water which had only brief contact with the rocks.

The electrical conductivity of water present values above 1500 µS / cm, these are mineralized waters that would have gone through gypsum/halite-licks (NaCl, $CaSO_4$ $2H_2O$, $CaSO_4$). This case is common in thermal springs Salihine, Kenif, and Djaarir, emerging in favor of the Triassic outcrops. The waters of cold springs are weakly mineralized and circulate in carbonate formations of the Albo-Aptian.

The mineralization is in agreement with the temperature of water. The thermal springs present the greatest values, the increase in water temperature involve dissolving minerals exceed 800mg / l.
[1, 20].

Chemical analysis of 13 samples show different contents of the elements assayed from one point to another. (table 1).

Table 1: Physicochemical characteristics of the water springs of the northern of the Aurès region. (May-2014).

	Geographic coordinats			Physical parameters				Cations (meq/l)				Anions (meq/l)			Saturation index			
Water springs	Lat.	Long.	Alt. (m)	pH	T°C	Mineralization (mg/L)	electrical conductivity µs/cm	Ca	K	Na	Mg	HCO3	Cl	SO4	SI. Calcite	SI. Dolomite	SI. Gypsum	S.I. Halite
H. Djaarir Sr1	35° 16' 45"	6° 47' 23"	1102	7.011	33.5	682	1681	5	0.53	16.7	1.07	2.64	20.94	0.93	-0.34	-0.21	-1.78	-5.21
Tafsaste Sr2	35° 18' 04 "	6° 38' 98"	1572	6.978	13	205	328	3.69	0.48	10.28	2.03	4.25	5	7.8	-0.25	-0.63	-0.97	-5.99
Ras El Ma Sr3	35° 18' 04 "	6° 37 '02"	1738	7.312	13	118	127.7	6.11	0.38	10.01	2.53	4.71	4	10.94	-0.01	-0.27	-0.63	-6.11
El Ma Lakhal Sr4	35° 21 ' 34"	6° 38 '34"	1329	7.742	14	144	271.1	5.72	0.47	6.42	3.75	3.26	2.41	9.88	-0.19	-0.42	-0.69	-6.52
Boulaghmène Sr5	35° 26 ' 49 "	6° 48' 98"	1158	6.981	15	286	538	5.31	0.43	6.47	4.75	3.4	2.31	10.84	-0.21	-0.33	-0.69	-6.50
Silène Sr6	35° 26' 02"	7° 05' 14"	1166	7.055	17	204	378	6.16	0.45	5.57	3.05	8.37	2.99	4.55	0.27	0.37	-0.97	-6.48
Manchare Sr7	35° 27' 46"	7° 08' 38"	1025	7.087	16	498	898	12.12	0.42	12.01	2.13	2.32	14.8	9.52	-0.06	-0.73	-0.44	-5.49
Karma Sr8	35° 26' 09"	7° 08' 19"	1147	7.154	17	504	509	9.3	0.22	9.6	0.86	14.53	4.04	0.98	0.68	0.45	-1.48	-6.11
H.Knif Sr9	35° 29' 11"	7° 15' 11"	1058	7.066	48	697	1860	6.23	1.44	16.18	3.09	3.46	20.96	1.16	-0.15	-0.46	-1.61	-5.26
H.Salihine Sr10	35° 26 ' 22"	7° 05' 06"	1071	7.801	65	819	2610	4.49	2.08	8.83	3.15	4.39	13	0.94	-0.15	-0.31	-1.8	-5.75
Zarif Sr11	35° 27' 12"	6° 54' 39"	1399	7.214	15	125	420	9.3	0.69	4.84	0.47	12.63	2	0.57	0.64	0.12	-1.68	-6.70
S'Fa Sr12	35°19'43"	7°02'10"	1190	7.381	16	144	271	4.25	3.55	4.96	0.6	10.28	1	1.5	0.23	-0.25	-1.57	-6.98
Mimoune Sr13	35° 22' 8"	6° 52' 54"	1175	7	16	178	476	9.26	0.68	4.95	0.61	13	2.11	0.57	0.65	0.25	-1.69	-6.67

3.2. *Chemical parameters*

3.2.1 *Chemical facies*

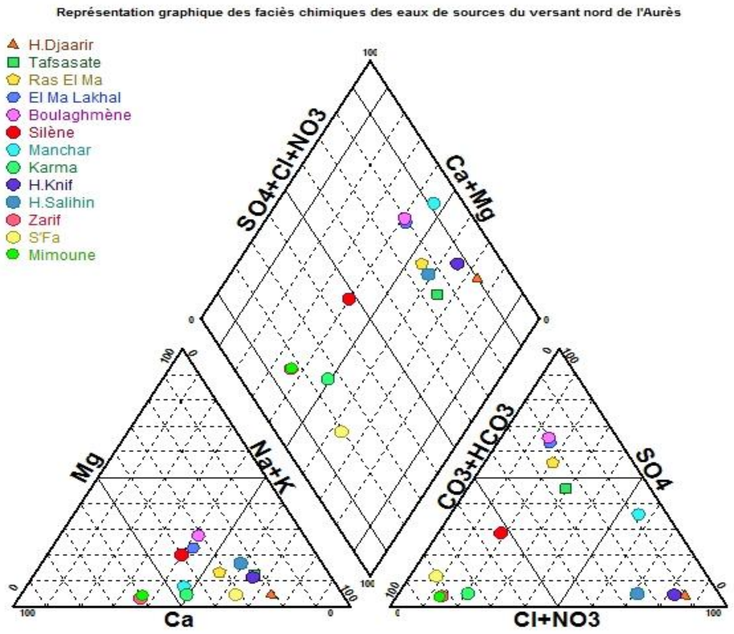

Figure 04: Chemical facies of water springs of the northern slope of the Aurès region (May-2014).

The data of the major ions carried over the Piper diagram allowed demonstrating the evolution of chemical facies water. The cold water of high-altitude exhibit a calcium bicarbonate facies, once these waters heated towards the piedmont of mountains, these waters evolves into calcium sulfated to chloride-sodium facies. (Fig. 4)

3.2.2. The origin of the minerals and the acquisition of the salinization

For better spatial and temporal characterization of the salinization phenomena of the carbonated aquifer, we studied the evolution of major elements according to the chloride ion that is a direct indicator of the origin of the water salinity and behaves as preserved element [1]. The interpretations of different diagrams lets identify brines from the dissolution of evaporites and the salinization related to the evaporation of water. (Fig.05).

Diagrams Ca^{2+} *vs* Cl^{-} (Fig.5.a) and Cl^{-} *vs* Mg^{2+} (Fig.5.b) show that the points are often located below the dissolution line. These basic exchange phenomena that characterize some aquifers levels of the massif of the Aurès region, are highlighted by the relationship $([Ca2^{+}+ Mg2^{+}) - (SO4^{2} + HCO3^{-})]$ and $[Na^{+}+ K^{+} -Cl^{-}])$ *vs* $[Na^{+}+ K^{+} - Cl^{-}])$ shown in (Fig5.f) [1, 7]. These exchanges result in the relationship plotted sample position. these basic exchange phenomena is carried out between the two parameters $([Ca^{2\,+}+ Mg^{2}+) - (SO_4^{2-} + HCO3^{-})]$ and $[Na^{+}+ K^{+} -Cl^{-}])$ helps to get rid of ions possibly from other reactions dissolution of carbonate and evaporite minerals [7]. In the absence of these databases exchange reactions, all the representative points of the samples must be placed near the point of origin [1, 7, 8]. The enrichment of Chloride observed can be attributed to anthropogenic activities. The relationship of Na^{+} *vs* Cl^{-} (Fig. 5.c) shows that the points are distributed to the line of halite dissolution contained in evaporite formations of the Triassic. The dots below the indicate dissolution of sodium depletion; this water is controlled mainly by cation exchange reactions between the water and red clays of the Pontien. They result in a fixation of the sodium and calcium release [9, 10, 13]. The report $SO4^{2}$- *vs* Cl^{-} (Fig.5.d) shows that the majority of water points are placed below the line and the SO_4 / Cl ratio is in favor of sulfates. One can suggest that this increase in the ratio is due to leaching and dissolution of gypsiferous inclusions. The return of irrigation water containing fertilizers is an additional source salinization of water bodies in the carbonate aquifer. [11, 12, 18]. The report $HCO3^{-}$ according to Cl^{-} (Fig.6.e) has a heterogeneous distribution of bicarbonates due to the spatial variation of the pH and gas exchange with the atmosphere. Excess bicarbonate demonstrates the dissolution of carbonate formations of the Cretaceous [1].

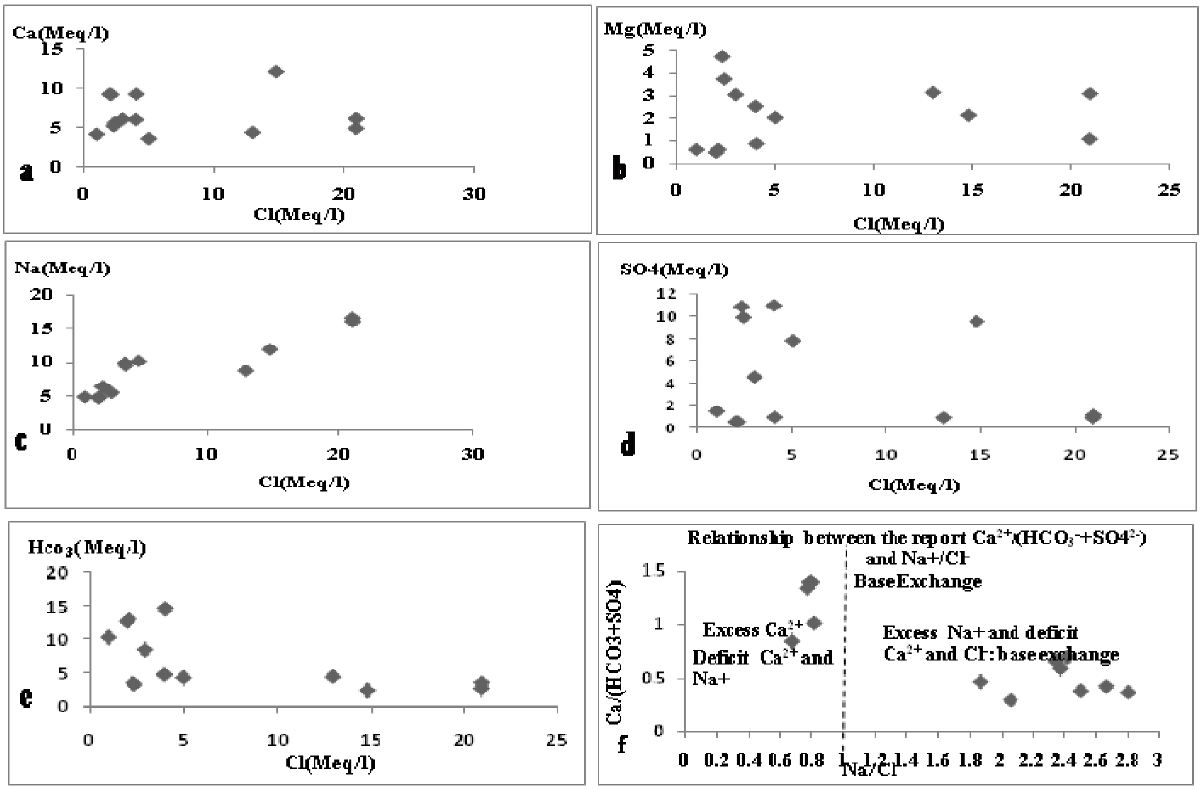

Fig.f.5. Relationship between the report ($Ca^{2+}/HCO3+SO4^{2-}$) and (Na^{+}/Cl^{-}) Of the springs water in the Auras- Algeria-

Figure 05: Changes in concentrations of the major elements according to the Chloride of water springs in the northern of the Aurès region. (May-2014).

3.2.3. Saturation Index of water samples

The calculation of the saturation index (SI) of water samples was performed with the PHREEQC software (USGS), (May-2014).

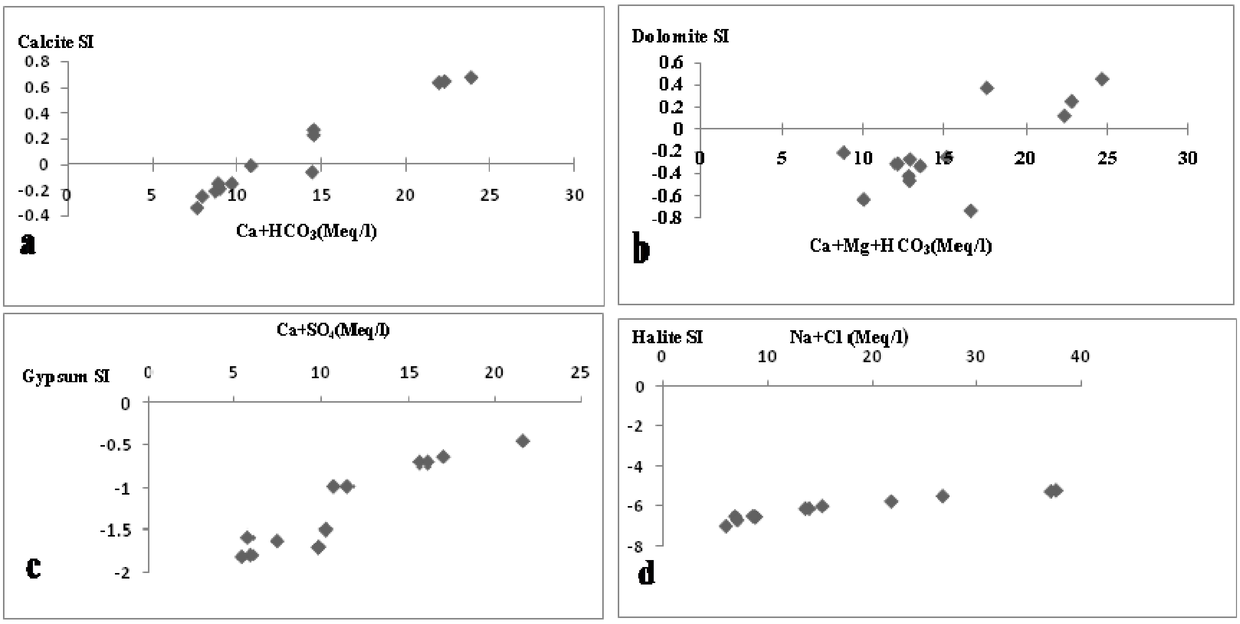

Figure 06: Correlation saturation indices values with respect to calcite, dolomite, gypsum and halite depending on Ca + HCO_3, Ca + Mg + HCO_3, Ca + $SO_4$and Na + Cl respectively.

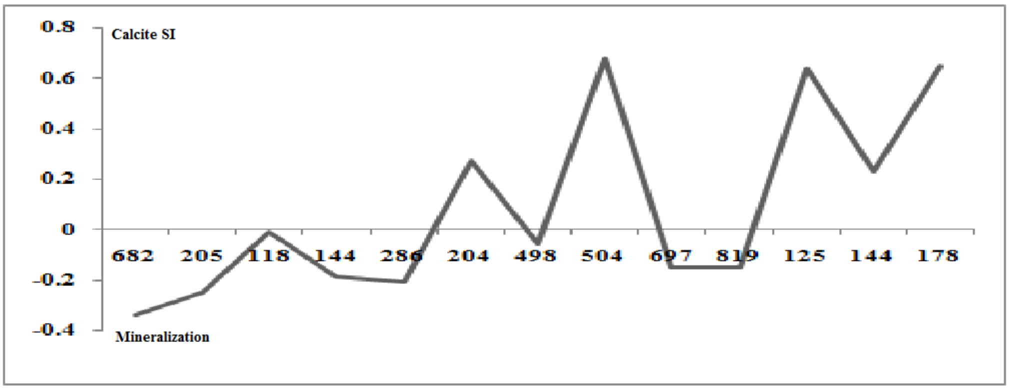

Figure 07: Changes in concentrations of the mineralization according to the saturation index of calcite of water springs in the northern of the Aurès region. (May-2014).

Saturation indices of calcite mineral (Fig 6.a) with respect to the mineral concerned shows an supersaturation state for most samples, illustrates the correlations between the calcite saturation index and ions concerned, this correlation confirmed the dissolution of carbonate minerals. Saturation index of dolomite mineral of mostly samples were negative (Fig.8.b) which also supports the hypothesis of the dissolution of this mineral in the water samples. The dissolution of gypsum (Fig.6.c) is confirmed through the inverse relationship between the saturation index of the mineral water and the sum of the ions from the eventual dissolution. There has been a close correlation between the saturation index of the Halite and ions (Ca + Cl) (Fig.8.d) is in a state of saturation, confirming the hypothesis of the dissolution of evaporites. Moreover, the salt leaching by rain events and the return of irrigation water favor the accumulation of salts in soils and contribute to the acquisition of the mineralization and to increase the salt content of water of water table. [10, 11, 15, 16]. The dissolution of carbonate and evaporate minerals is as the reactions [14]:

- Calcite: $CaCO3 + H2O <==> Ca^+ + HCO\ 3^- + OH^-$
- Dolomite: $CaMg\ (CO3)_2 + 2CO_2\ (g) + 2H_2O <==> Ca^+ + Mg^+ + 4HCO^-$
- Gypsum: $CaSO_4 + 2H_2O <==> Ca^+ + SO_4 + 2H_2O$
- Halite: $NaCl <=====> Na^+ + Cl^-$

Figure 7 shows that the waters are moving towards high positive values of saturation index (up to 0.7). At these values should precipitate of the calcite and saturation index cap; confirming the precipitation of calcite.

This figure shows the spatial evolution of the mineralization. The lowest values of the mineralization characterize cold water deposits, and appear to be related to rapid infiltration of rainwater at the limestone formations, sulfated and bicarbonate, and also to the low temperature. The greatest values of the mineralization characterize hot water deposits (Hammam El SalihineSR10, Hammam El Kenif SR9 and Hammam Djaarir SR1). The increase in water temperature involves dissolving minerals exceed 800mg / l, is in perfect agreement with the temperature of the depth of the earth.

3.3. Application of principal components analysis ACP

The ACP, applied on the physico-chemical parameters, confirms the results on the origin of the salinity obtained previously. The study of the spectrum of own values shows that there are three areas to be used for the interpretation of results since they hold 80% of the information. In the variable space, the axis F1 appears as a mineralization factor (Fig.9) on which are positively correlated most of the elements (EC, mineralization, Ca^{2+}, Na^+, Cl^-, Mg^{2+} and $SO4^{2-}$.), It explains 50% of the total variance. Note a very significant correlation between the parameters EC, mineralization and T (°C); features thermal springs. This factor axis represents 50% of the variance, which is low considering the number of sample; the selected parameters, the major elements and salinity parameters. This result is consistent with the Piper diagrams that do not show a well defined chemical evolution. Both results indicate a strong heterogeneity of facies from water and geochemical pathways in the process of acquisition of mineralization. This shows heterogeneity (thermal / non-thermal) and it is due probably by the lithology.

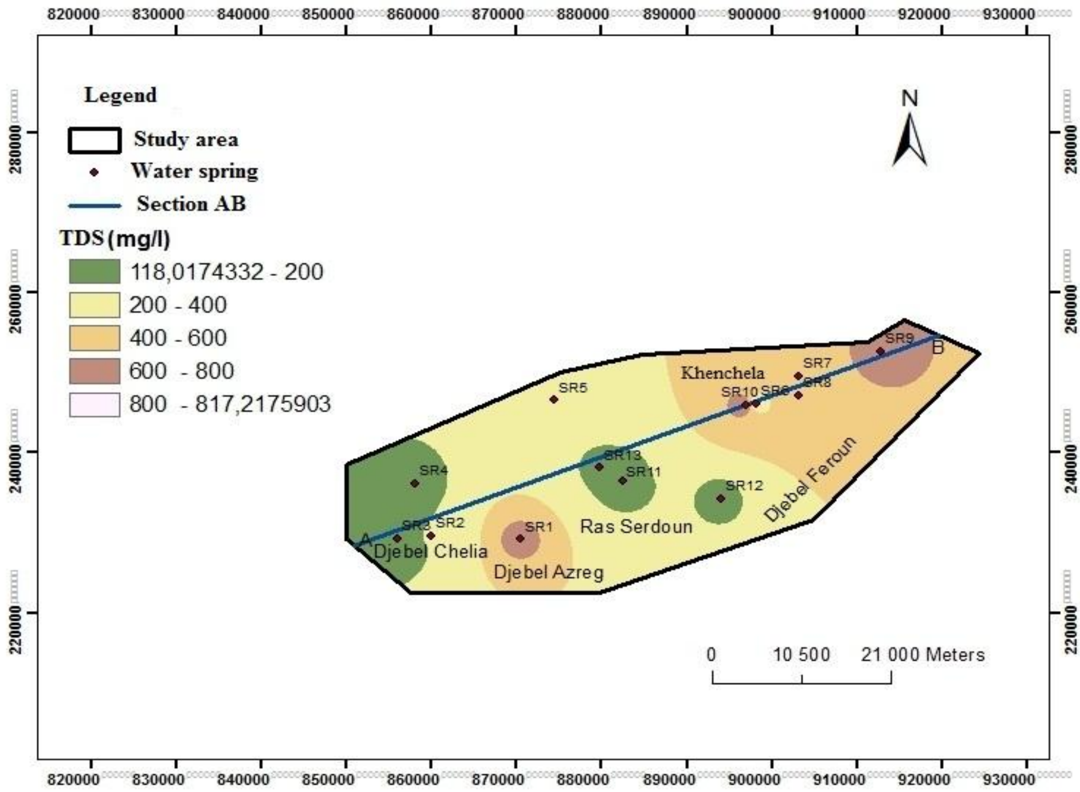

Figure 08: Spatial distribution of total mineralization of water springs in northern massif of the Aurès region (May- 2014).

Table 02: Correlation matrix of the variables adopted for CPA.

Variables	pH	T°C	TDS (mg/L)	EC (µs/cm)	Ca	K	Na	Mg	HCO3	Cl	SO4
pH	**1**										
T°C	0.369	**1**									
TDS (mg/L)	0.086	**0.848**	**1**								
CE (µs/cm)	0.239	**0.964**	**0.927**	**1**							
Ca	-0.255	-0.284	-0.018	-0.165	**1**						
K	0.408	0.389	0.122	0.274	-0.397	**1**					
Na	-0.250	0.457	**0.713**	0.576	-0.049	-0.156	**1**				
Mg	0.214	0.203	0.120	0.165	-0.345	-0.187	0.050	**1**			
HCO3	-0.111	-0.305	-0.348	-0.384	0.362	0.100	-0.560	-0.674	**1**		
Cl	-0.108	0.687	**0.853**	**0.808**	0.006	0.028	**0.906**	0.073	-0.561	**1**	
SO4	0.017	-0.468	-0.384	-0.435	-0.054	-0.419	-0.059	0.632	-0.573	-0.236	**1**

Numbers in bold indicate significant correlations.

The factorial F2 axis expresses 21% of the total inertia; it will oppose the bicarbonate waters sulfated waters. These are recent and superficial waters which differ from the warm deep waters. The significance of the second factorial axis is probably due to the lithological heterogeneity (opposition facies carbonate / sulphate constant facies mineral).
The factorial axis F3 expresses 16% of the total inertia; it will oppose the thermal waters that have the chemical facies sodium chloride. (Table 3)

Table3: Own values of the first three axes CPA.

Axis component	F1	F2	F3
Own value	5.849	2.683	2.009
Variability (%)	44.993	20.636	15.455
Cumulative%	44.993	65.628	81.084

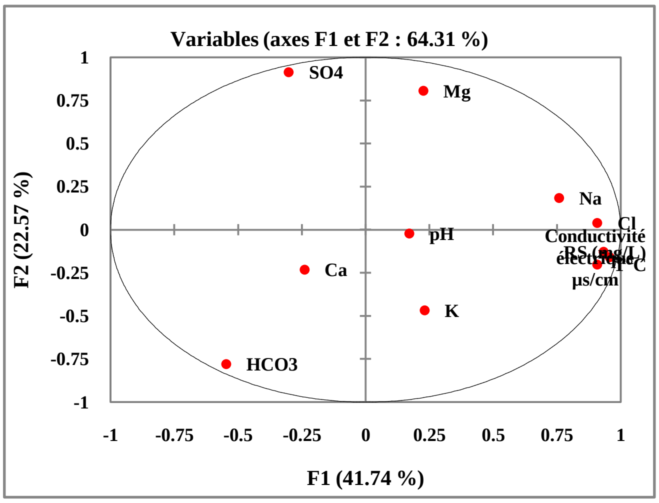

Figure 09: Projected variables of water springs.

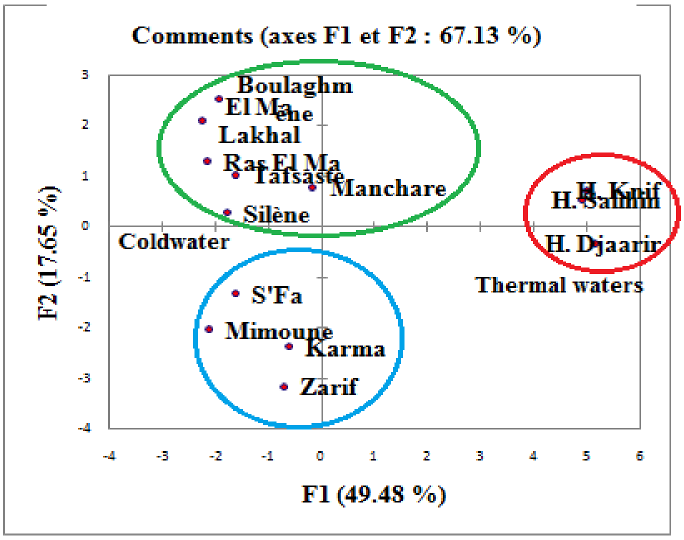

Figure 10: individual projection of water springs.

Figure 10 shows the three water types: calcium bicarbonate waters, chlorinated sodic; intermediate mixed water type and calcium chloride-sulfated. The cold surface waters at high altitudes have calcium bicarbonate water, once heated in depth foothills of the mountains, these waters evolves into calcium chloride-sodium sulfated water.

Conclusion

The results of this study help to understand the mechanisms of acquisition of mineralization of water Cretaceous and Pliocene-Quaternary aquifers in the North slope of the Aurès region. These mechanisms are as follows:
- Interaction water-rock: the more or less prolonged circulation of water in the aquifer of carbonated nature and the yield sediments of the wadi: Triassic and carbonate deposits of the Cretaceous are accompanied by water-rock interaction with the phenomenon of dissolution and therefore cause an increase in the mineralization of waters.
- Anthropogenic (agricultural): evaporation from the soil surface and in the first horizons after irrigation causes a gradual increase in salinity of the solutions of the unsaturated zone. The infiltration of irrigation and effective rain water loaded with salts and chlorides that are especially highly mobile ions, contributes to the increased salinity spring waters of the northern slope of the Aurès. The effect of over-exploitation in areas of high agricultural activity that use the waters of the lower strata are generally more mineralized. [10].

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