

HYDROGEOCHEMISTRY OF GROUNDWATER IN ES-SBIKHAT EL-MAHMEL BASIN, KHENCHELA (NE ALGERIA)

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ABSTRACT

Es-Sbikhat El-Mahmel basin, located at the southeastern piedmont of Aures massif (Northeastern Algeria), is characterized by a semi-arid condition. The sampling process was realized within 39 boreholes and wells during May 2015. Results of analysis data projected on the PCA (Principal Component Analysis) plan, which express 52.70% of variance has shown a chemical facies evolution from calcium-bicarbonate water into calcium-chloride water, going through a transition facies marked by calcium-sulfate to magnesium-sulfate water.

Thermodynamic analysis corroborated that water-rock interaction is the main process that control mineralization (dissolution-precipitation, cationic exchange and anthropogenic pollution).

Keywords: Mineralization, Pollution, Thermodynamic, Es-Sbikhat El-Mahmel basin, PCA.

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1. INTRODUCTION

The groundwater is the main source of water supply in arid and semi-arid regions. Their quality is controlled by natural context and anthropogenic factors that limit their exploitation. The interaction of these factors results in various water types [1].

Major elements variations in the groundwater are controlled by cation exchanges, dissolution



and precipitation of minerals, evaporation and oxidation-reduction reactions. These complicated hydrogeochemical processes help to get an insight into the contributions of rock-water interaction (geochemical study) that influences groundwater quality. These geochemical processes are responsible for the seasonal and spatial variations in groundwater chemistry [2].

The knowledge of hydro-chemical process is essential to determine the origin of mineralization of groundwater. Importance of hydrochemistry of groundwater has led to a number of detailed studies on geochemical evolution of groundwaters [3-7]

The objective of this research is to investigate various factors that influence water hydrogeochemistry.

2. THE STUDY AREA

2.1 Geographical location

Es-Sbikhat El-Mahmel Bassin is extended over 343.54 km² of area. It is a shared territory between several physical units, whose totality belongs to the Atlas region of Aures-Nemamcha Mountains [8]. (Figure 1)

This perimeter develops the best agricultural soils, except for some salt grounds developed around the Sebka called « Bahiret Esbikha ». Its altitude is on the average of 1060 m [8].

The basin is surrounded by several mountains: Chataia mountains (1455 m) and their continuation, Tafrent mountains (1405 m), Aidel mountains (2000 m) and its continuation, Chelia mountains (2328 m), Djahfa mountains (1700 m), Koudiat Seguigine and Tadelist (1599 m) and Tadinart mountains (1374 m). In addition, it is crossed by many Oueds such as Es- Sbikhaoued and Zoui.

Interpretation of climate data shows that the area is on the semi-arid domain with an average annual rainfall of 487.6 mm and temperatures ranging between 6°C and 27°C.

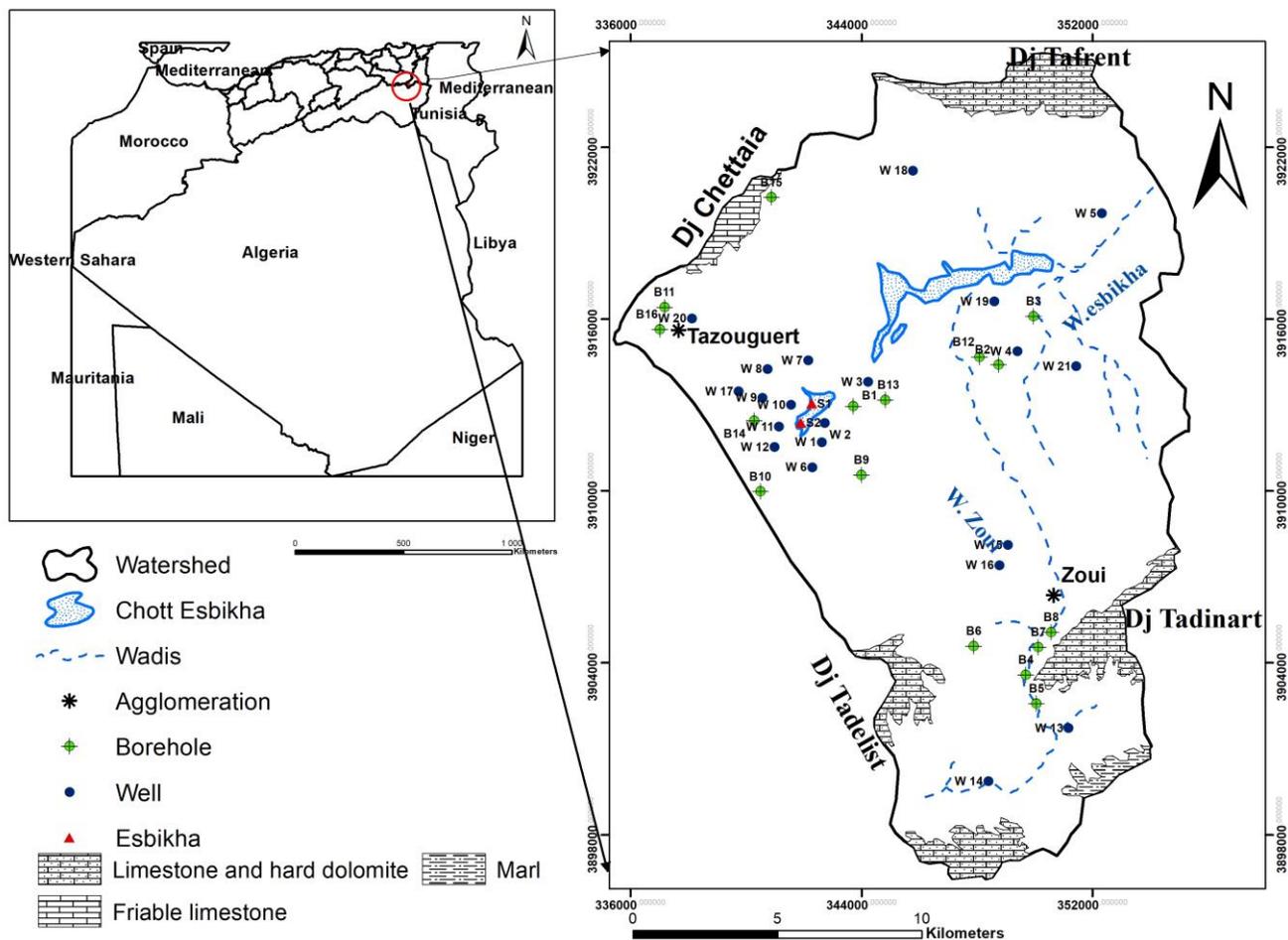


Fig.1. Location of the studied area and the sampling sites

2.2 Geological and hydrogeological settings

Geologically, the studied area is a sedimentary basin filled with erosion deposits, whose stratigraphic series are Cenomanian marls at the base, with 700 m of thickness, surmounted by Turonian marls and limestones having 150 m of thickness, on which rests a limestone formation having 100 m of thickness, representing the Maastrichtian. At the top, there are deposits of sand, silt and gravels with big pebbles representing the Quaternary [9]. (figure2).

From the hydrogeological point of view, we can identify two important aquifers; the first is superficial (50 m) and the second is deeper (150 m) [9].

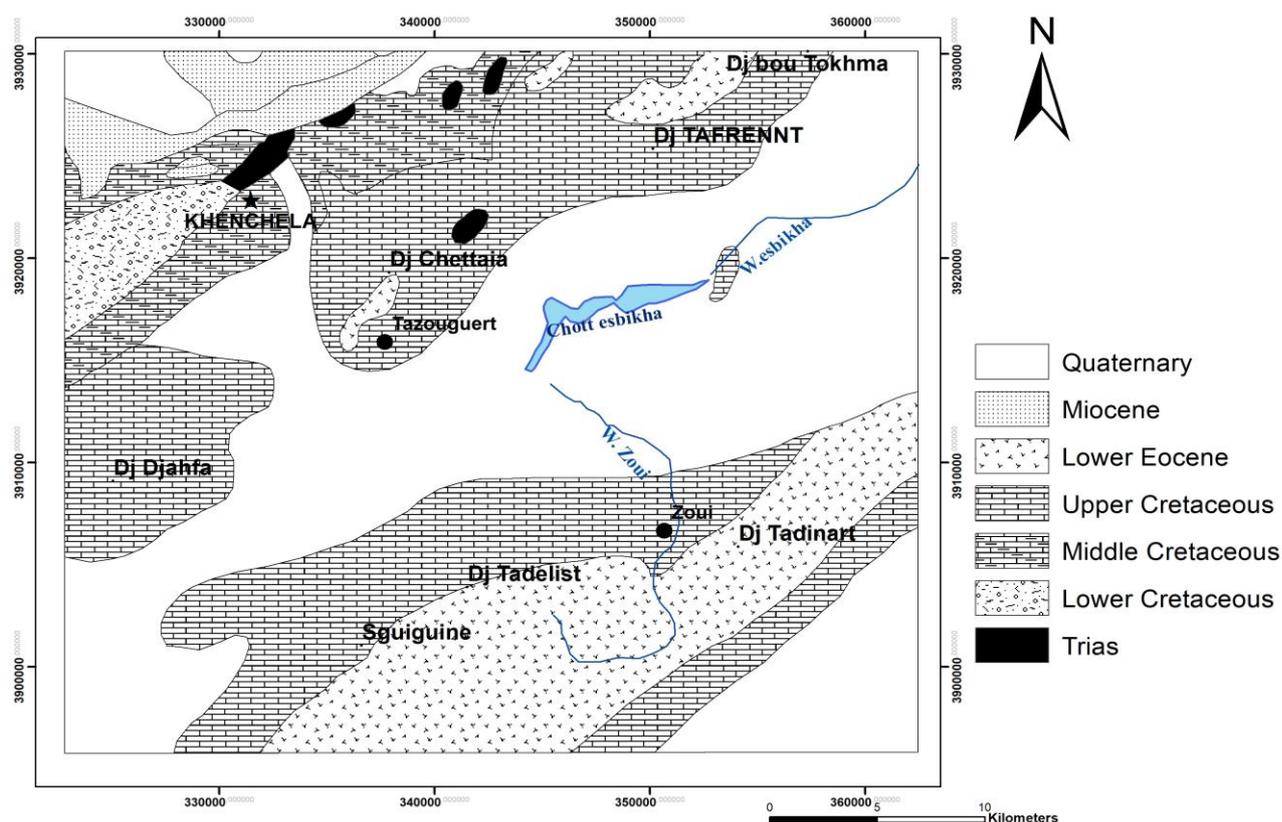


Fig.2. Geological context

3. MATERIAL AND METHODS

A sampling campaign on Es-Sbikhat-El-Mahmel groundwater and surface resources (Figure 1) is realised during May 2015 in which 39 samples were collected. Physicochemical analysis (electrical conductivity, pH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , SO_4^{2-} and NO_3^-) were at the laboratory of Earth Sciences Faculty (Constantine University), compatibly with standard techniques which details are shown in table 1.

Table 1. Physico-chemistry methods

Parameter	unit	protocols
Temperature	°C	Thermometer
Electrical conductivity	$\mu\text{S}/\text{cm}$	Conductivity-meter
pH	/	pH-meter
Sulfates, Nitrates SO_4^{2-} and NO_3^-	mg/l	Visible-UV spectrophotometer
Magnesium, Sodium, Potassium Mg^{2+} , Na^+ , K^+ ,		Flame spectrophotometer
Chlorides Cl^- ,		Titrimetry
Calcium Ca^{2+} ,		EDTA complexometry

Analysis results reliability were checked by applying the ionic balance method, and permissible error doesn't exceed 10%.

ArcGis software (version 10.1) enabled us to make the basin mapping. The chemical facies is determined by Diagrammes software 6.5 (LHA – Avignon). The index of saturation (SI) was calculated with PHREEQC software. The PCA (Principal Component Analysis) projection was carried using XLSTAT 2014.

4. RESULTS AND DISCUSSION

4.1. Chemical facies types

Piper diagram is largely used in the hydrochemical classification of waters [11], (Figure 4). The points cloud shows an evolution of hydrochemistry, from calcium–bicarbonate type in outcrops downstream of the basin and calcium– sulfate to calcium–chloride types in the irrigated perimeters and upstream behind the Sebkh. Some waters are magnesium–sulfate type (Figure 5).

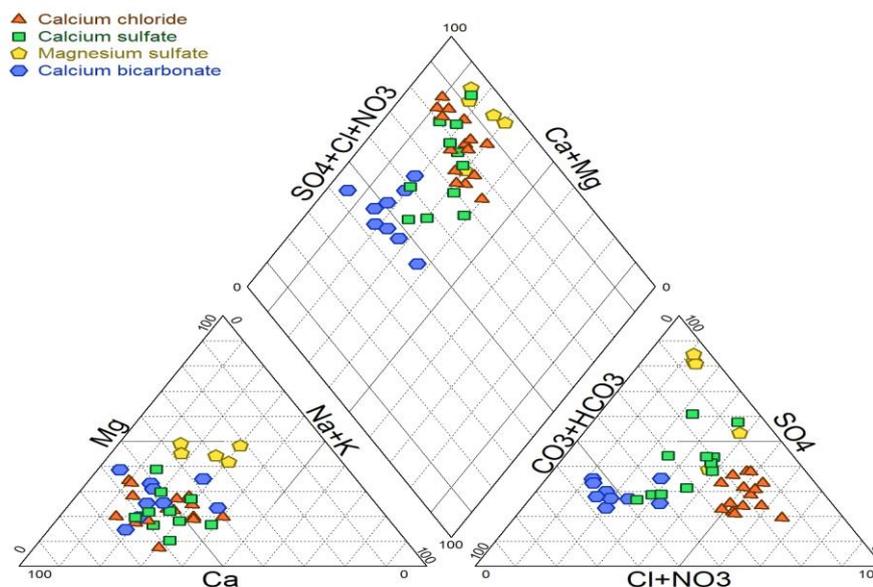


Fig.3. Piper diagram

4.2. Statistical results

Statistics on 37 individuals (boreholes and wells) and 11 variables (Temperature, electrical conductivity, pH, Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , HCO_3^- , SO_4^{2-} and NO_3^-) allows ordering data to extract maximum information about the main factors involved in the simultaneous evolution of variables and their mutual relationship [12].

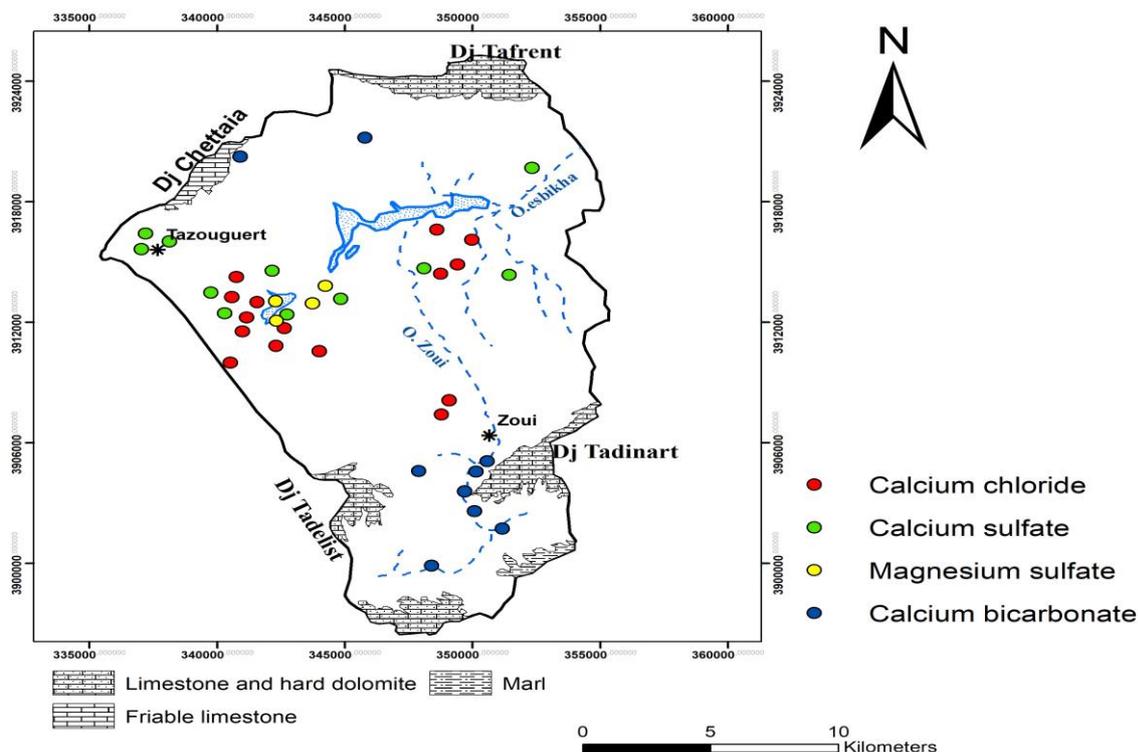


Fig.4. Distribution map of chemical facies

4.2.1. Basic statistics

Table 1 sums up the statistical parameters of physicochemical characteristics of water points monitored and analyzed.

Table 2. Physicochemical parameters of studied waters

Variable	T°	EC	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
Unit	°C	μS/cm	/	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l	mg/l
Minimum	16	460	6.5	64.13	14.16	8.97	0.024	128.1	17.75	88	0.3
Maximum	20	4560	8.1	376.76	237.12	169.05	6.16	414.8	513.75	1035	128
Mean	18.13	1678.92	7.21	161.29	51.13	80.84	1.82	234.59	199.23	284.38	51.78
SD	1.08	1016.59	0.28	89.98	44.78	40.53	1.65	67.46	130.48	235.18	27.22
VC	0.06	0.61	0.04	0.56	0.88	0.5	0.91	0.29	0.65	0.83	0.53

4.2.2. Correlations matrix

The correlation between variables in groundwaters helps comprehend certain phenomena of water-rock interactions. It allows us to know about the common origin of certain parameters

[13].

Positive correlations for all our water points were determined from the correlation coefficient (Table 2).

According to Mangin criterion, A [14], the critical coefficient is 0.568, for the 37 individuals and at the threshold of 5 %.

Table 3. Correlation matrix of variables

Variables	T°	EC	pH	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	HCO ₃ ⁻	Cl ⁻	SO ₄ ²⁻	NO ₃ ⁻
T°	1										
EC	-0.0251	1									
pH	-0.2390	-0.2918	1								
Ca ²⁺	0.0421	0.7595	-0.4524	1							
Mg ²⁺	-0.0946	0.7971	-0.3047	0.6038	1						
Na ⁺	0.0565	0.7659	-0.0692	0.5974	0.5951	1					
K ⁺	-0.1232	0.8336	0.0684	0.5841	0.6519	0.8958	1				
HCO ₃ ⁻	-0.0215	0.2502	-0.0522	0.0398	0.1050	0.3174	0.2800	1			
Cl ⁻	-0.0443	0.9008	-0.2521	0.7558	0.7134	0.7367	0.7910	-0.0345	1		
SO ₄ ²⁻	0.0372	0.7863	-0.3883	0.8427	0.8257	0.7168	0.6771	0.1414	0.6695	1	
NO ₃ ⁻	0.1885	0.4521	-0.1313	0.5966	0.2162	0.2944	0.3367	-0.4056	0.5406	0.4010	1

Values in bold indicate significant correlations

4.2.3 Factorial designs analysis

This analysis has been pushed up to 3 factors, presenting 78.87 % of the total variance (Table 4).

Table 4. Proper values and percentages expressed for principal axes

	F1	F2	F3
Proper value	5.80	1.62	1.26
Variability (%)	52.70	14.73	11.44
Cumulative %	52.70	67.43	78.87

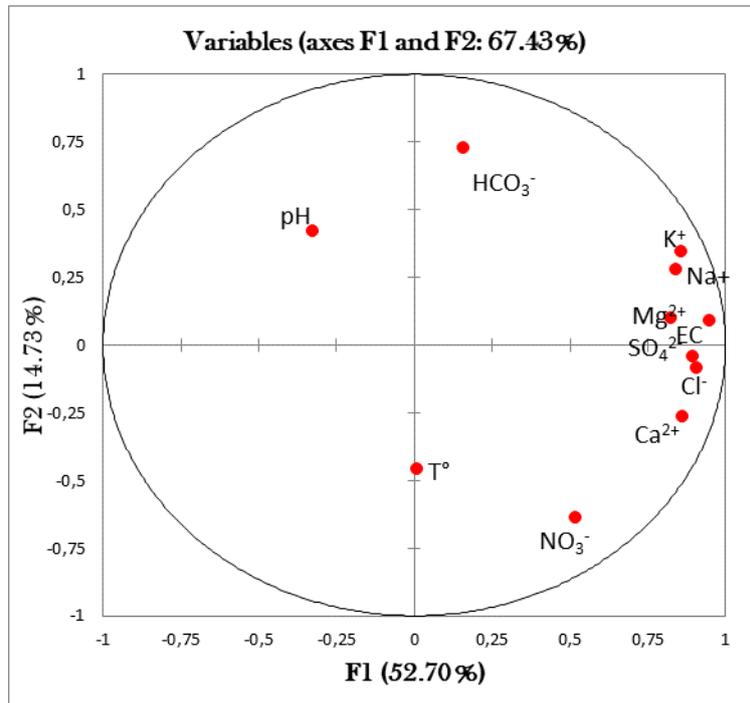


Fig.5. Analysis in the variables space (factorial design F1-F2)

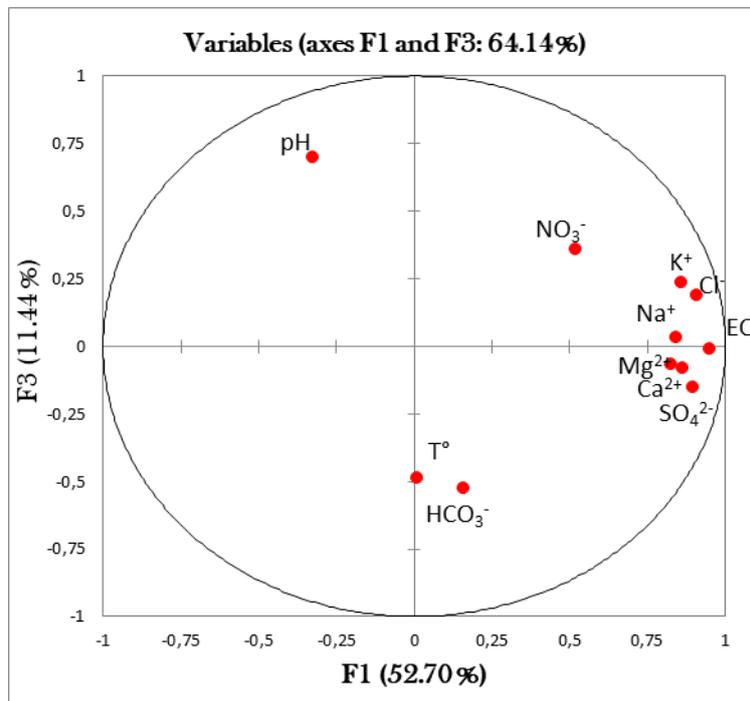


Fig.6. Analysis in the variables space (factorial design F1-F3)

F1 axis (52.70 % of variance) is the mineralization pole and groups the variables: electrical conductivity, Cl^- , Na^+ , Mg^{2+} , Ca^{2+} , SO_4^{2-} and K^+ (Figure 6).

F2 axis (14.73 % of variance) in which nitrates are negatively correlated and bicarbonates are positively correlated (+0.75): F2 opposes nitrate pollution (anthropogenic origin: fertilizer) and an intrinsic origin (dissolution of the reservoir rock) (Figure 6).

The F3 axis (11.44 % of variance), is determined by pH (Figure 7), it represents strongly influenced waters by the dissolution of the carbonate formations of the Jurassic.

4.3 Origin of salinity

Major elements are represented as a function of chloride ion (conserved element) to characterize the origin of water salinity.

The groundwater of different samples shows in general enrichment in Ca^{2+} , SO_4^{2-} , and poverty in Na^+ , K^+ and Mg^{2+} . The major reactions which enrich or improve water of the chemical elements are the Ca^{2+} - Mg^{2+} exchange due to the interaction carbonated water-rocks, the basic exchange Na^+ - Ca^{2+} or Na^+ - Mg^{2+} and the reduction of sulfates dissolution [15] in [7].

The graph Na^+ vs Cl^- (Figure 9 A) shows that all the groundwater samples are plotted under the mixing line of fresh and saline water. Considering that Na^+ content should balance Cl^- content, the Na^+ deficit is explained by the basic ionic exchange phenomenon between water and the aquifer, which led to Na^+ adsorption by clayey phase and a release of Ca^{2+} [7]. The graph Ca^{2+} vs Cl^- (Figure 9 B) corroborates the enrichment in calcium. This contribution is due to the simultaneous dissolution of carbonates and gypsum, associated with Ca^{2+} contribution through the cationic exchange. The water-rock interaction phenomenon essentially explained the simultaneous enrichment in Ca^{2+} and the impoverishment in Mg^{2+} (Figure 9 C) as dolomitization, dissolution and precipitation [17] and [18] in [4].

The relation between SO_4^{2-} and Cl^- (Figure 9 D) shows that the major groundwater samples are plotted above the mixing line of fresh and saline water except for some points, which are around this line. Sulfates enrichment would be due to contribution through gypsum dissolution, leaching of evaporates and infiltration of irrigation water.

The relation between the couple K^+/Cl^- (Figure 9 E) emphasizes that all samples are plotted

under the mixing line, showing probable pollution origin.

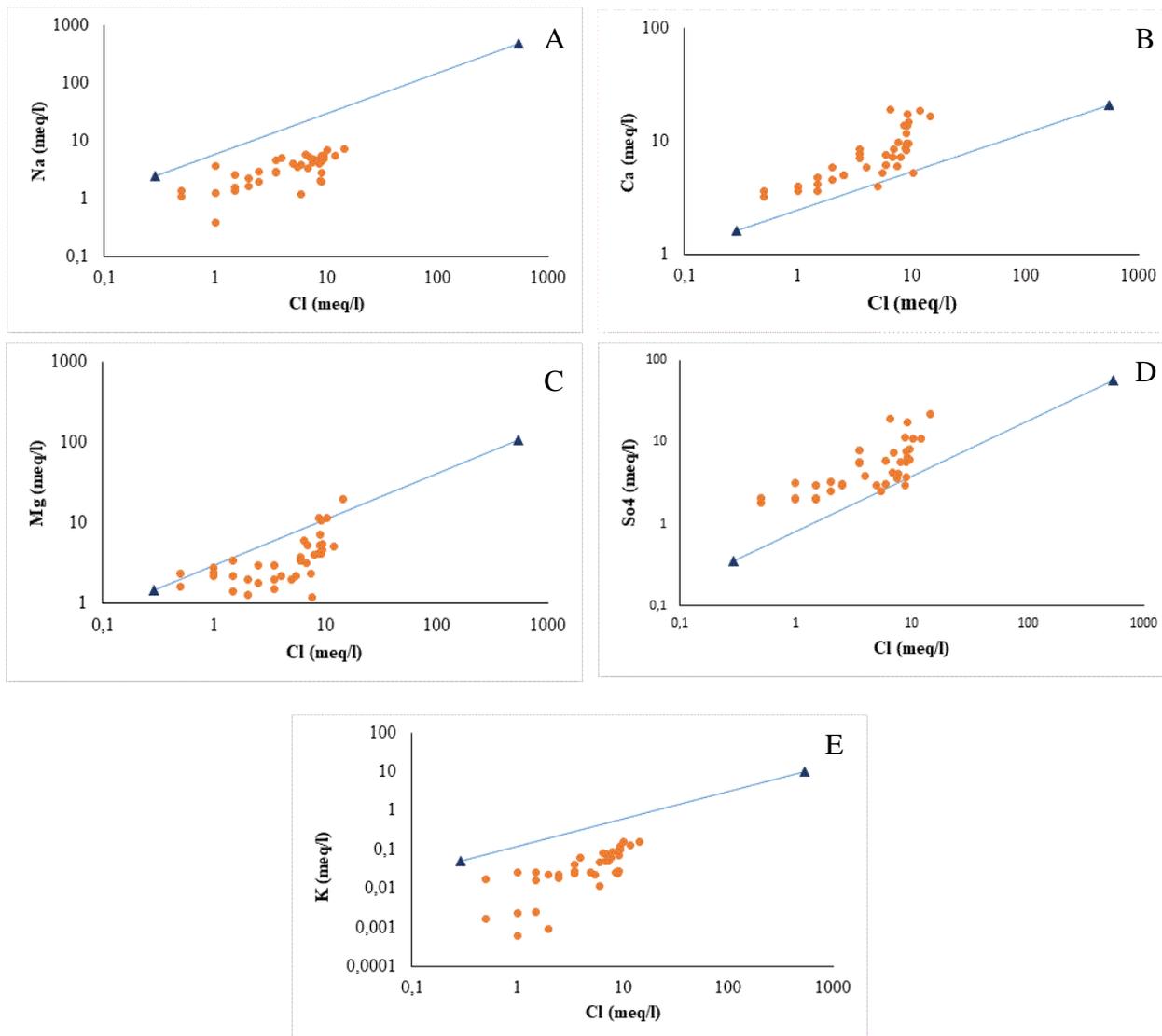


Fig.7. Relations Na⁺, Ca²⁺, Mg⁺², SO₄²⁻, K⁺ and Cl⁻ of groundwaters

4.4. Saturation index and solution-minerals equilibria

Water/rock Interactions control hydrogeochemistry. Mineral equilibrium calculation can predict the thermodynamic control on the composition of groundwater that has equilibrated with various minerals [1]; [19]; [20].

The degree of saturation can be evaluated according to the following equation:

$$SI = \log\left(\frac{KIAP}{Ksp}\right) \tag{1}$$

SI<0 means undersaturated groundwater

SI>0 means supersaturated groundwater. [21] and [22] in [23].

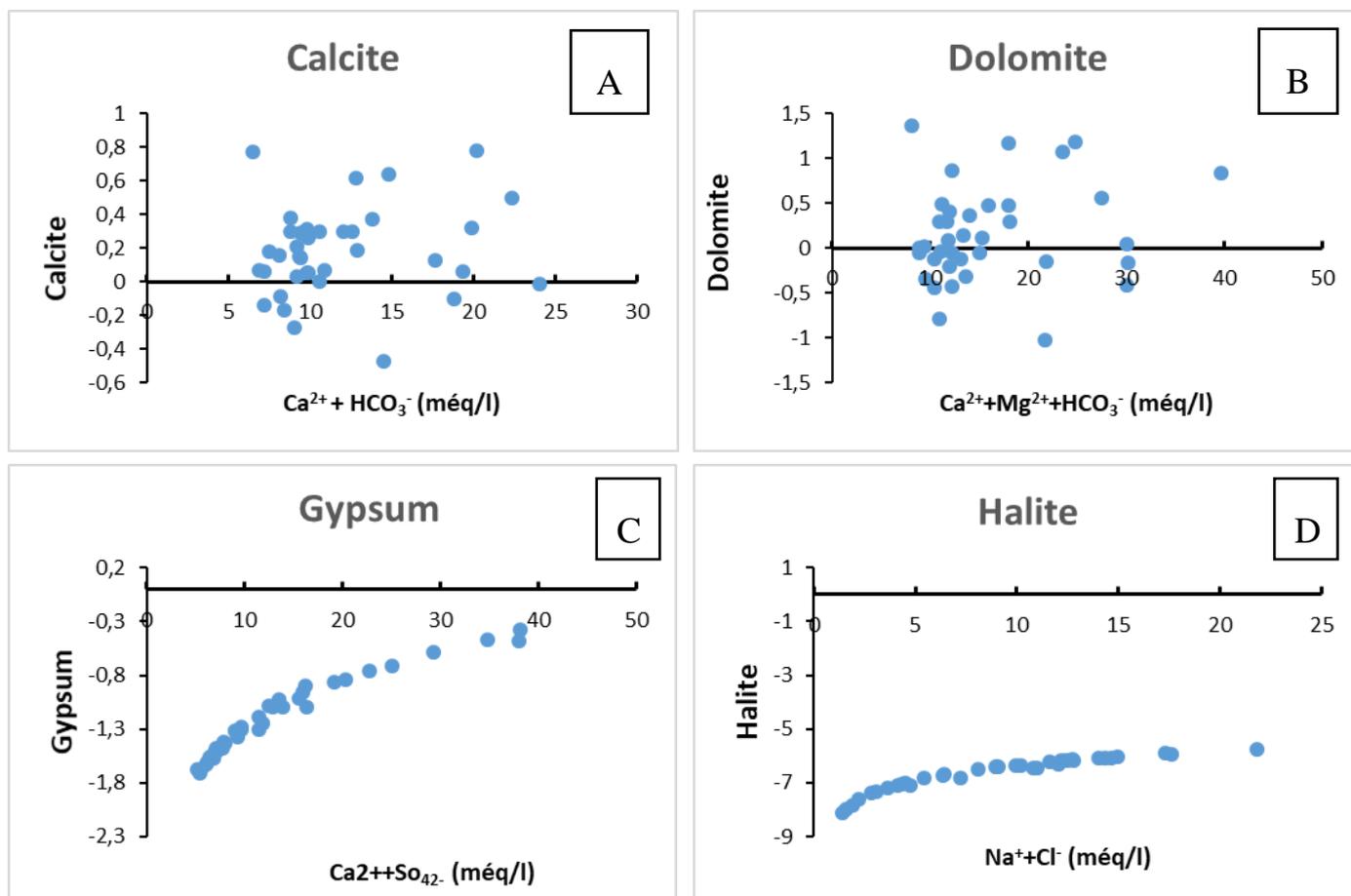


Fig.8. Saturation indices correlation with major components

Calcite and dolomite saturation indices with minerals show a saturation state for most of the samples (Figure 10 A and 10 B), which highlights the precipitation of these minerals in water, but they are rather undersaturated as regards halite and gypsum (Figure 10 C and 10 D). Saturation index of minerals in water points out that only the carbonate minerals tend to precipitate, especially under the form of dolomite. In contrast, the evaporitic minerals are in dissolution state, which induces an undersaturation of the solution.

4. CONCLUSION

This study demonstrates the interest of coupling thermodynamic with geochemistry and statistical tools to study the evolution of hydrochemistry of Plio-quadernary water. Piper

diagram has shown a chemical composition evolution from bicarbonate-calcium water in the calcareous outcrops into chloride-calcium waters downstream of the basin at the limits of the Sebkhah, going through a transition facies marked by sulfate-calcium to sulfate-magnesium waters in the Plio-Quaternary filling. The PCA projection reveals three factors which explained 78.87% of the variance in the entire data set. Factor 1 identifies the mineralization pole. Factor 2 opposes nitrate pollution and an intrinsic origin. Factor 3 represents samples strongly influenced by carbonate formations dissolution of the Jurassic.

The binary diagrams demonstrate that waters mineralization is related to water-rock interaction through the geochemical process of mineral dissolution-precipitation, cationic exchange and anthropogenic pollution. Thermodynamic analysis, of solution-minerals equilibria, has revealed that the solution is marked by a carbonate saturation, calcite and dolomite (CO₂ degassing) and dissolution of evaporitic formations, gypsum and halite marked.

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