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Hydrochemical and statistical characterization of groundwater in the Chemora area, Northeastern Algeria

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ABSTRACT

This work aims to evaluate the hydrochemical characteristics of a shallow aquifer located between carbonated formations and salt lake in the Chemora region in northeastern Algeria. Hydrochemical, multivariate statistical, and the thermodynamics techniques were used to investigate the hydrochemical evolution within the aquifer. Twenty-five water samples were collected during May 2013 in this the aquifer wells. The results indicate that this shallow water is characterized by sulfate-dominant facies representing about 64% of cases, followed by the chloride with 24%, and the remaining (12%) is represented by the bicarbonate facies. The sulfate facies is acquired mainly by the alteration of pyrite. The saturation index showed that all carbonate minerals are supersaturated and all evaporate minerals are undersaturated which suggest that their soluble component Na^+, Cl^-, Ca^{2+}, and SO_4^{2-} concentrations are not limited by mineral equilibrium. The application of the cluster analysis and the principal components analysis based on major ion contents defined 3 main chemical water types reflecting different hydrochemical processes with salinity increases along the groundwater flow.

Keywords: Cluster analysis; Factor analysis; Hydrochemistry; Salinity; Algeria

1. Introduction

The groundwater quality is influenced by many factors, such as the chemistry of infiltration water, topography, geology of the reservoir rock, and anthropogenic factors [1]. These factors lead to a variation in the chemical composition and hydrogeochemical facies. The dissolution of minerals from the surrounding rock into water is the dominant factor controlling the chemical composition of these waters. Some minerals such as carbonates and evaporates are rapidly dissolved and significantly change the water chemical composition, while other minerals such as silicates dissolve more slowly and therefore have less effect on water chemical composition [2]. The presence of a salt lake hydraulically connected to groundwater also changes the water salinity by reversing the flow to groundwater due to overexploitation of the latter [3]. This intrusion of water highly mineralized from a salt lake has been reported in other regions undergoing a semi-arid climate as in Algeria [4]. Temperature

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also has an important role in controlling the chemical and biological composition of a freshwater body [5,6]. Temperature plays a catalytic role in the various chemical and biological reactions. It thus increases the speed of the chemical reaction and allows the dissolution of large quantities of minerals. All these phenomena occur along groundwater flow depending in part of the residence time which controls the evolution of groundwater chemical composition [7]. These hydrochemical processes are the result of the rock–water interaction and anthropogenic affecting the chemical quality of groundwater [8,9]. Note that these geochemical processes are responsible for the seasonal and spatial variation of groundwater geochemical quality [10,11]. Knowing these hydrochemical processes is fundamental to determine the origin of groundwater chemical composition. Numerous studies on groundwater quality have been made in this region aiming to understand the mechanisms responsible of this geochemical typology [12–17].

Multivariate statistical techniques, cluster analysis (CA), and principal component analysis (PCA) are effective means of computing, interpreting, and representing data relative to groundwater pollutants and geochemistry. They are frequently used to characterize the quality of groundwater [18] and adopted PCA to assess groundwater quality in a Blackfoot disease area in Taiwan. Two factors, seawater salinization and arsenic pollutant, were also considered and their factor scores were mapped [19] and applied the PCA to distinguish several groundwater signatures, including uncontaminated groundwater, agricultural activities, mining activities, and sewage pollution [20,21]. The CA was used to discuss the geochemical evolution, mineralization, and groundwater contamination. Additionally, the CA was also used to interpret the hydrochemical data based on factor scores [22–24]. The hydrogeochemical study of the groundwater evolution was attempted by [25] using the factor analysis. This allowed determining that sea water intrusion, weathering process, and leaching of secondary salt dominant factors controlling groundwater geochemistry.

Several techniques have been applied to assess and characterize the chemical changes in groundwater, such as thermodynamic equilibrium that define the chemical equilibrium of groundwater. For this, the tendency of chemical forms between dissolved and inorganic phase was examined by the saturation index. This expresses the degree of chemical equilibrium between water and the inorganic matrix in the aquifer and can be considered as a measure of dissolution and/or precipitation in the of water-rock interaction [26,27]. The use of code PHREEQC [28], allows calculating the saturation indexes of carbonate minerals (aragonite, calcite, and dolomite) and evaporating minerals (anhydrite, gypsum, and halite).

The main objective of this work is to assess the chemistry of groundwater and identifying the main geological processes that controls the geochemical evolution of groundwater in the region of Chemora.

2. Materials and methods

2.1. Natural conditions

The region of Chemora is a relatively flat area with very low slope. This plain has an average altitude of 890 m and surrounded by reliefs culminating at 1,250 m. This morphology allowed the installation of a low endorheic hydrographic network. The main river, Wadi Boulhilet powers the salt lake (Garaet Onk Djemel) by surface water especially during heavy thunderstorms. The climate of the region is semi-arid, with an annual average rainfall of about 270 mm and an annual average temperature of 13.2°C [29]. This semi-arid behavior essentially is due to irregular rainfall, exposing the region to increased temperature and high evapotranspiration provoking a loss of water balances that exceed 420 mm/year [29]. The geological formations found in the region are Aptian age. They are constituted at the base of limestone, dolomite, and sandstone at the top of clays and gypsum marl. The Mio-Plio-Quaternary age includes at the base of red clay gypsum sometimes surmounted by lacustrine limestones, conglomerates, and alluvium [30]. The salt mineral formations sequence is dominated by gypsum ($CaSO_4{\cdot}2H_2O$), thenardite (Na_2SO_4), glauberite ($Na_2Ca{\cdot}(SO_4)_2$), dolomite ($CaMg\ (CO_3)_2$), mirabilite ($Na_2SO_4{\cdot}10H_2O$), halite (NaCl), quartz (SiO_2), and epsomite ($MgSO_4{\cdot}7H_2O$) in association with pyrite (FeS_2) [30].

Tectonics of the region has resulted in the formation of a broad syncline filled with Mio-Plio-Quaternary deposits. The superposition of several tectonic phases generates in the development of severe fault network of N020–N050 and N100–N120 [30].

The hydrogeological study of the area showed the existence of a shallow aquifer located in the Mio-Plio-Quaternary alluvial formations based on clay, marl, and sometimes gypsum [31]. This study showed that the shallow aquifer is unconfined in association with the salt lake. The thickness of the aquifer can reach 80 m in the center of the plain. These alluvial deposits have an average permeability of 10^{-4} m/s [31]. The piezometric investigation showed that since 2007 the water table has kept the same structure. The high piezometric gradient observed in the Fedjoudj chain decreased regularly toward the north and the northwest, indicating the importance of this chain in the recharge of shallow aquifers (those located near the Fedjoudj piedmont). This piezometric situation is also characterized by the presence of a flow to the north in the western part of the groundwater and southeast, northwest, and northeast in the Eastern part of the groundwater. It also indicates the presence of a piezometric depression limited between the salt lake and carbonate formations, discharging by Wadi Boulhilet and a reverse flow from the salt lake to the groundwater (Fig. 1). This tendency was possible due to the lowering of groundwater. During wet years, the salt lakes of the region constitute a discharge zone. By cons in dry periods, and with the increase in operating wells, there is a lowering of the water table. The area is known by industrial agriculture that strongly tolerates salt [31]. This situation has led to an imbalance in the hydrogeological system and caused a reversal of flow. This is currently observed in the region as it has been shown in previous studies by [3,32].

2.2. Sampling and analysis techniques

Twenty-five samples were collected during the month of May 2013 in order to examine the evolution of physicochemical parameters. These samples were taken in wells at 15 min during pumping after stabilizing water temperature in order to remove groundwater stored in the hydraulic structure. These samples were taken using two polypropylene bottles washed with acid. Each sample was immediately filtered *in situ* through 0.45-μm filters on the cellulosic acetate. Filtrate for cations analyses were transferred into 100 cm^3 polyethylene bottles and immediately acidified to pH < 2 by the addition of Merck™ ultrapure nitric acid (5 ml 6 N HNO_3). Samples for anions analyses were collected into 250-cm^3 polyethylene bottles and were not acidified. All samples were stored in an ice chest at a temperature of <4˚C and transferred later to the laboratory of the National Agency for Water Resources of Constantine and stored in a refrigerator at a temperature of <4˚C until they have been analyzed (within 1 week). Immediately after sampling, pH and temperature (*T*˚C) were measured *in situ* using a multi-parameter WTW (P3 MultiLine pH/LF-SET). The analyzed chemical elements are calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na^+), potassium (K^+), chloride (Cl^-), bicarbonate (HCO_3^-), sulfate (SO_4^{2-}), and dry residue (DR). This was achieved using standard methods as suggested by the American Public Health Association [33]. Table 1. The respective ionic balance is generally around 10%.

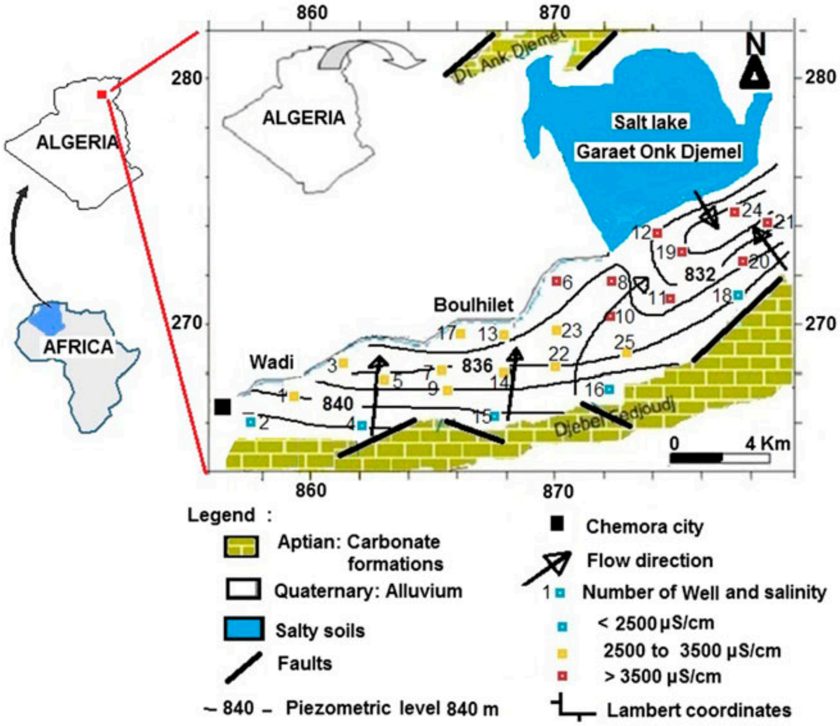

Fig. 1. Hydrogeological map of the study area.

Table 1
Statistical parameters of the chemical elements in groundwater superficial aquifer. Min: minimum; Max: maximum; SD: standard deviation; CV: coefficient of variation. Concentrations in mg/l, T in ˚C and EC in µS/cm

Variables	Min	Mean	Max	SD	CV	WHO
T (˚C)	19.10	19.46	19.90	0.19	0.01	25
pH	6.70	7.10	7.70	0.30	0.04	7–8.5
EC	1,010.00	3,647.60	10,120.00	2,065.84	0.57	750
Ca^{2+}	72.14	243.55	609.21	126.60	0.52	75
Mg^{2+}	51.72	145.48	536.88	107.54	0.74	50
Na^{+}	42.60	138.54	265.80	63.72	0.46	50
K^{+}	1.80	8.10	16.50	3.65	0.45	12
HCO_3^-	225.70	355.12	463.60	58.50	0.16	/
Cl^-	99.40	292.54	340.80	62.89	0.21	200
SO_4^{2-}	145.00	803.40	3,580.00	768.02	0.96	200
NO_3^-	0.20	7.36	38.50	10.11	1.37	50

3. Methodology

The thermodynamics analysis was conducted using the code PHREEQC [28] to compute the saturation indices (SI) and tackle speciation minerals. The calculation of the SI was conducted according to Eq. (1).

$$\mathrm{IS} = \log\left(\mathrm{IAP}/K\right) \qquad (1)$$

where IAP is the ion activity and K, the equilibrium constant. The SI minerals are used to evaluate the state of saturation of the water and controlling the chemistry and equilibrium with the solid phase [27]. In general, the water–rock equilibrium is reached when $\mathrm{SI} = 0$. If $\mathrm{SI} > 0$, water is supposed supersaturated, precipitation of minerals is necessary to reach the equilibrium, by against if $\mathrm{SI} < 0$, water is undersaturated, dissolution of minerals is necessary to reach equilibrium [34]. For carbonates [35], believes that a solution is saturated with carbonates when $\mathrm{SI} > 0.2$ and is undersaturated with bicarbonate when $\mathrm{SI} < 0.2$ as the computation of this index may be affected with a relative error of 50%. Therefore, these minerals control the chemistry of these waters.

All mathematical, multivariate analysis and statistical computations were made using Excel 2010 (Microsoft Office®) and STATISTICA 6 (StatSoft, Inc.®). Multivariate analysis of the lake groundwater quality data-set was performed through CA and the PCA.

The PCA was also applied to the treatment of these chemical data. Although PCA is an exploratory and descriptive method, the treatment aims to identify the main factors that control the chemistry of groundwater [36]. This multivariate statistical method has been widely applied to investigate the phenomena of the environment across the world [37–39] and in Algeria [11–17,40–42]. These tools multivariate statistics were used successfully to study the hydrogeochemical processes [16,43–46]. This work deals with the force of multivariate techniques to characterize hydrochemical variations in the Chemora area.

CA comprises a series of multivariate methods which are used to find true groups of data or stations. In clustering, the objects are grouped such that similar objects fall into the same class [47]. The hierarchical method of CA, which is used in this study, has the advantage of not demanding any prior knowledge of the number of clusters, which the nonhierarchical method does. A review by Sharma [48] suggests Ward's clustering procedure to be the best, because it yields a larger proportion of correct classified observations than do most other methods. Hence, Ward's clustering procedure is used in this study. As a distance measure, the squared Euclidean distance was used, which is one of the most commonly adopted measures [49]. In the present work, CA was applied using the Euclidian distance as a distance measure between samples and Ward's method as a linkage rule for classification of the hydrogeochemical data of the area Chemora.

4. Results and discussion

4.1. General hydrochemistry

Obtained results show that mean temperature of water was 19.46˚C. The examination of the chemical analysis shows that the pH varies between 6.7 and 7.7, indicating that water has a low alkalinity. It is known that the process of buffering calcite and dolomite, are dominant in the pH range 6.5–7.5 [50]. The pH measured for the 25 groundwater analyzed samples are found in this range for 92% of cases. The electrical conductivity (EC) values range from 1,010 to

10,120 µS/cm. The order of abundance of the major cations is $Mg^{2+} > Ca^{2+} > Na^{+}$ and almost all samples exceeded the maximum acceptable concentration of Ca for drinking water (75 mg/l) except sample no 16, however all samples exceeded the maximum acceptable concentration of Mg for drinking water (50 mg/l). The abundance of the major anions is $SO_4^{2-} > Cl^{-} > HCO_3^{-}$ and almost all samples exceeded the maximum acceptable concentration of Cl^{-} for drinking water (200 mg/l) except two samples nos 4 and 16, but all samples exceeded the maximum acceptable concentration of SO_4^{2-} for drinking water (200 mg/l) [51].

The dominant elements give a global magnesium sulfate facies type. The plot of the chemical analyses in the Piper diagram [52] shows in the anions triangle, a clear trend against sulfates and on the other side, the cations triangle shows only a slight magnesium influence (Fig. 2). The facies detailed examination illustrates that the sulfated facies represents 64% of cases, followed by chlorinated facies with 24%, and the rest (12%) is represented by the bicarbonate facies. The first two facies are linked with salty formations of salt lake marl and clay licks, while the third is in connection with the carbonate facies formations located on the boundaries of the aquifer which correspond to the limits of recharge. This facies typology stresses the complexity of the hydrochemical processes that govern the salinity of this groundwater. The presence of fractured and karstified limestone formations on the southern and eastern boundaries led to prediction of the infiltration of rainfall allowing it to acquire their original bicarbonate mineralization. The molar ratio Ca^{2+}/Mg^{2+} of samples collected near the southern and eastern limits is <2, indicating the dissolution of carbonates [53]. This also explains the presence of low salinity (<2,500 µS/cm) of water in these limits. These waters are in advantage mineralized in SO_4^{2-} in contact with the salt in liaison with the salt lake and terrigenous formations, of the aquifer formations. This is occurring by weathering the salt and salty mineral along the groundwater flow.

Two distinct origins of SO_4^{2-} are clearly highlighted: the first is the oxidation of pyrite, and the second is the dissolution of gypsum and epsomite [54]. Oxidation of pyrite can be occurred in the presence of carbonates allowing environmental enrichment in Ca^{2+}, Mg^{2+}, and SO_4^{2-} by reactions (2)–(4) [55–58]. These reactions make it possible to lead, from one (1) mole of FeS_2, at two (2) moles of SO_4^{2-} and two (2) moles of Ca^{2+}, if pyrite is neutralized by the calcite. Otherwise, if pyrite is neutralized by dolomite, the reaction allows reaching at two (2) moles of SO_4^{2-}, one (1) mole of Ca^{2+} and one (1) mole of Mg^{2+}.

$$FeS_2 + 3.75O_{2(aq)} + 1.5H_2O_{(aq)} \rightarrow Fe(OH)_{3(S)} + 2SO_4^{2-} + 4H^{+} \tag{2}$$

$$FeS_2 + 2CaCO_3 + 3.75O_2 + 1.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + 2Ca^{2+} + 2CO_2 \tag{3}$$

$$FeS_2 + CaMg(CO_3)_2 + 3.75O_2 + 1.5H_2O \rightarrow Fe(OH)_3 + 2SO_4^{2-} + Ca^{2+} + Mg^{2+} + 2CO_2 \tag{4}$$

The presence of the evaporate sequence in association with the salt lake allows the dissolution of epsomite ($MgSO_4$ $7H_2O$) according to reaction (5) and gypsum according to reaction (6) [56].

$$MgSO_4 \cdot 7H_2O \rightarrow Mg^{2+} + SO_4^{2-} + 7H_2O \tag{5}$$

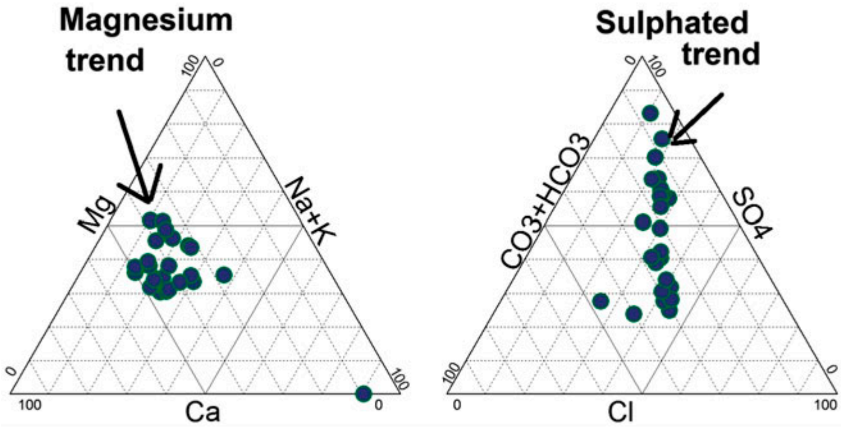

Fig. 2. Piper diagram Piper applied to Chemora groundwater.

$$CaSO_4 \cdot 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O \quad (6)$$

These dissolutions allow from one (1) mole of $MgSO_4$, to lead to one (1) mole of Mg^{2+} and one (1) mole of SO_4^{2-} and from one (1) mole of $CaSO_4 \cdot 2H_2O$, to one (1) mole of Ca^{2+} and one (1) mole of SO_4^{2-}. In the two cases, the molar ratio of Ca^{2+}/Mg^{2+} is equal 1.

The alteration of pyrite in the presence of carbonates allows to provide the hydrochemical system, four (4) moles of SO_4^{2-}, three (3) moles of Ca^{2+}, and one (1) mole of Mg^{2+}. So the molar ratio Ca^{2+}/SO_4^{2-} would be 0.75 and the molar ration Mg^{2+}/SO_4^{2-} would be 0.25 which give a molar ratio Mg^{2+}/Ca^{2+} in the whole hydrochemical system equal to 1:3.

Fig. 3 shows the evolution of SO_4^{2-} with Ca^{2+} and Mg^{2+} in the groundwater of Chemora region. Those elements were found highly correlated which allowed to have very significant positive coefficients of determination (0.85 and 0.94). This shows that the concentrations of the three elements proportionally increase in the Chemora aquifer. The trend slopes are very close to the theoretical molar ratio of the alteration of pyrite and not gypsum reports. As Figs. 4 and 5 reveal that the plot of Ca^{2+} vs. Mg^{2+} and the liaison $Ca^{2+} + Mg^{2+}$ vs. SO_4^{2-} are highly significant (0.78 and 0.95) and the slopes of the straight patterns are on the order of 1, thereby that the system is in equilibrium. This allows saying that the presence of the Ca^{2+}, Mg^{2+}, and SO_4^{2-} in Chemora groundwater seems to be also due to the dissolution of gypsum and/or anhydrite. While infiltration of water in carbonate formations located in the south and east, the dissolution of carbonates is done according to the reactions (7)–(9). The slight difference between the various molar ratios and slopes of various straight would be due to the complexity of chemical reactions.

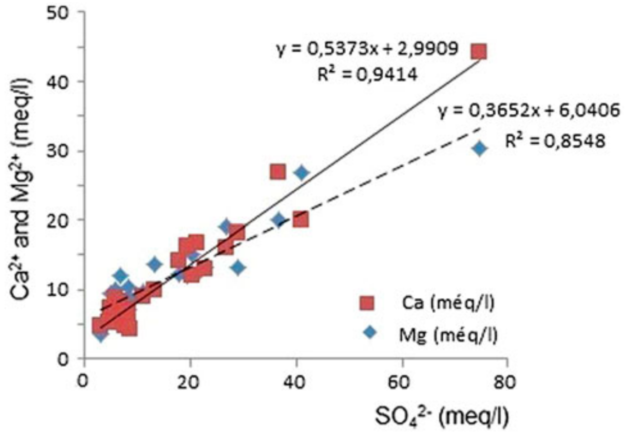

Fig. 3. Relationship Ca^{2+}, Mg^{2+} vs. SO_4^{2-} in groundwater Chemora.

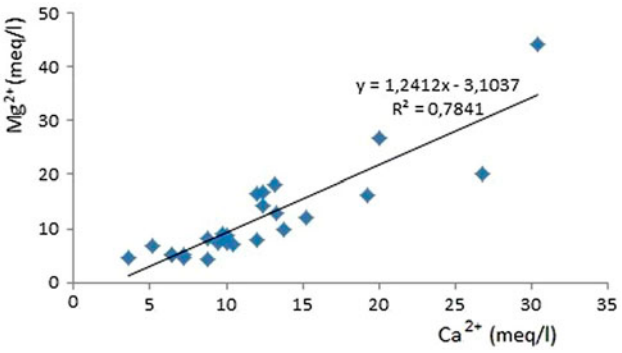

Fig. 4. Relationship Ca^{2+} vs. Mg^{2+} in groundwater Chemora.

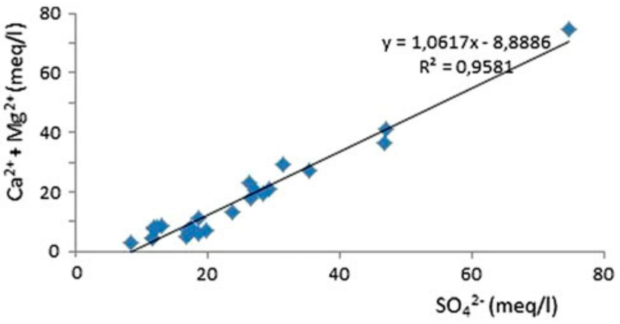

Fig. 5. Relationship $Ca^{2+} + Mg^{2+}$ vs. SO_4^{2-} in groundwater Chemora.

$$CO_2 + H_2O \rightarrow H_2CO_3 \quad (7)$$

$$H_2CO_3 + CaCO_3 \rightarrow Ca^{2+} + 2HCO_3^- \quad (8)$$

$$2H_2CO_3 + CaMg(CO_3)_2 \rightarrow Ca^{2+} + Mg^{2+} + 4HCO_3^- \quad (9)$$

These dissolution phenomena were also studied using thermodynamics that controls the water composition. The calculations provided SI of minerals that might be reacting in the system. The saturation calculations show that all carbonate mineral groups are supersaturated with respect to aragonite, calcite, and dolomite. Adversely, all evaporate mineral groups; anhydrite, gypsum, and halite are undersaturated in all groups suggesting that their soluble component Na^+, Cl^-, Ca^{2+}, and SO_4^{2-} concentrations are not limited by the mineral equilibrium (Fig. 6).

4.2. Cluster analysis (CA)

Two different methods can be applied to identify clusters, including R- or Q-modes. R-mode is usually applied to water quality variables to reveal the interactions between them, while Q-mode reveals the interactions between the studied samples. The advantage of using the hierarchical method of CA applied in this work is not requesting any prior knowledge of the number of cluster [59]. Here, CA was applied using the Euclidian distance as a distance measured between samples and Ward's method as a linkage rule for classification of the hydrogeochemical issued from Chemora area. Nine hydrochemical measured variables (EC, Ca, Mg, Na, K, Cl, SO_4, HCO_3, and NO_3) were utilized in this analysis. For statistical purpose, all the variables were log-transformed and more closely correspond to normally distributed data. Subsequently, they were standardized to their standard scores (z-scores) as described by [39].

As there is no test to determine the optimum number of groups in the data-set [39], the visual inspection is the only criteria to select the groups in the dendrogram (Fig. 7). The defined phenon line [60] was chosen at a linkage distance of 250. At this distance, the groups could be distinguished in terms of their hydrochemical variables. As shown in Fig. 7, nine variables were classified into three clusters. These groups are: group 1 (G1) Ca and HCO_3, group 2 (G2) Na, Cl, and K and group 3 (G3) CE, SO_4, Mg, and NO_3. The G1 with low salinity (EC < 2,500 μS/cm), G3 with high salinity (EC > 3,500 μS/cm), and G2 with intermediate and average salinity (2,500 < CE < 3,500 μS/cm). The first group is made up of 5 wells represented by samples nos 2, 4, 15, 16, and 18, and concerns 25% of the water samples. This type of water is relatively fresh with a mean EC of 1,724 μS/cm, which is the characteristic of less saline water and it is influenced only by the Aptian carbonate facies outcrops characterized by Ca and HCO_3. This groundwater (G1) in the studied area can be classified as recharge area waters.

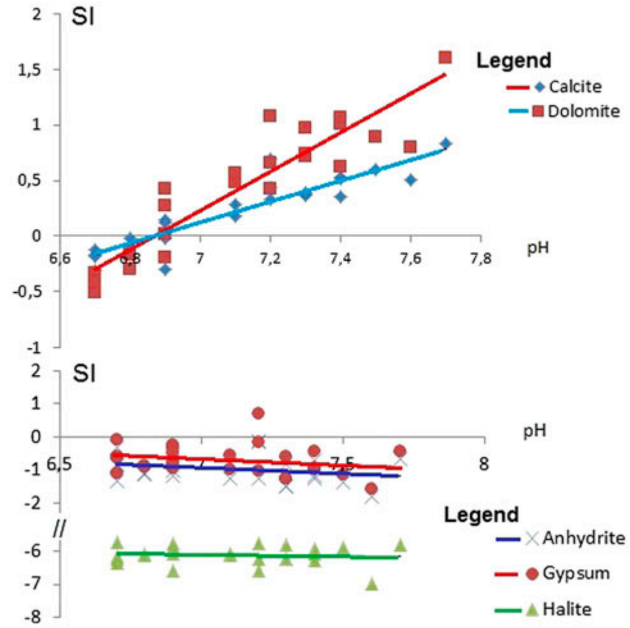

Fig. 6. Variation of the saturation index of carbonate minerals in the groundwater of Chemora.

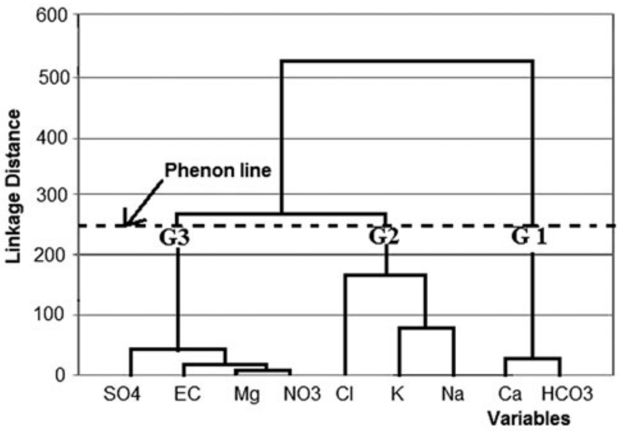

Fig. 7. Cluster dendogram for variables.

Group 2 is represented by the wells 1, 3, 5, 7, 9, 13, 14, 17, 22, 23, and 25, and it occupies 44% of the water samples. The EC for this group is 2,754 μS/cm, which is the characteristic of mixed water (Na–Cl–K). This water type can be interpreted as the first step of water–rock interactions occurring in dilute solutions, explained by the abundance of evaporite formations in the aquifer. This group constitutes a transition area waters between the two extreme groups G1 and G3 and it is characterized by an enrichment of Na and Cl (Fig. 8).

The third group is made up of 9 wells represented by samples nos 6, 8, 10, 11, 12, 19, 20, 21, and 24 where the EC is 5,898 μS/cm which is the characteristic of blended water. This group is located near the salt lake where evaporation is intense and it is characterized by SO_4 and Mg. This groundwater for G3 is considered as discharge area water. Based on geological and geographical situation, discharges of urban and industrial wastewater, and contamination of the groundwater by water of salt lake explains the high concentrations. The dissolution of the Triassic evaporate formations (halite) could be responsible for this elevation.

This logic of succession (G1–G2–G3) is in agreement with the flow direction that allows the concentration of elements in the rows and lines of groundwater flow.

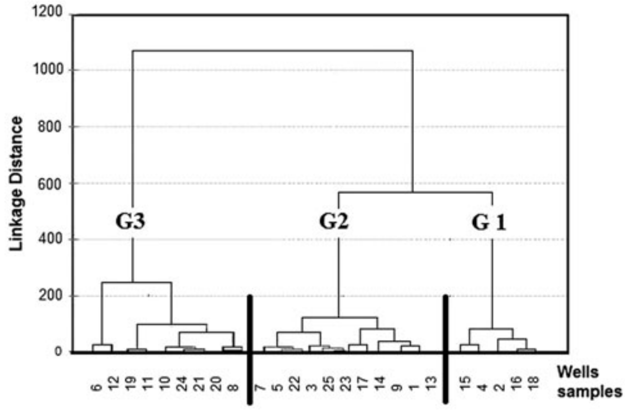

Fig. 8. Cluster dendogram for water samples.

4.3. Principal component analysis (PCA)

The PCA analysis is centered reduced performed on a table of 25 individuals and 9 variables (EC, Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-}, and NO_3^{-}). The first result of this analysis is the correlation between the different variables. The correlation coefficient is commonly used to estimate the relationship between two variables. It is a simple statistical tool to show the degree of connection between the various variables. The correlation matrix outcome of the PCA shows that EC has a significant relationship (0.60–0.94) with Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, and SO_4^{2-}. This reflects the participation of these elements in the acquisition of saline load of groundwater in the region. Ca^{2+} and Mg^{2+} show a strong positive correlation (>0.80) with SO_4^{2-}, indicating a probable common origin. Na^{+} and Cl^{-} (0.65) have also a pretty good positive connection. These strong bonds may suggest the dissolution of chloride salts, sulfate and sulfide as pyrite or marcasite minerals [61].

The second result of this analysis is the liaison between the different variables and individuals because it is used to examine the underlying patterns for a large number of variables and then to determine the possible contributing factors in the waters samples hydrochemistry [62,63]. The Kaiser criterion [64] was applied to determine the total number of significant factors. An examination of the Kaiser–Meyer–Olkin (0.705) measure of sampling adequacy suggested that the sample was factorable. The eigenvalues for different factors, accounted percentage variance accounted, cumulative percentage variance, and loadings component loadings (Varimax rotated) are given in Table 2. According to this criterion, only factors that eigenvalue greater than or equal to 1 have been retained as a possible source of variance in the data. The reason for choosing 1 is that a factor should have a variance at least as large as that of a single standardized original variable to be acceptable. Four principal factors (*F*) were extracted and rotated using the varimax normalization [64]. Two factors (*F*1 and *F*2) were selected after varimax rotation and represent more than 73% of the total variance, which is quite good and can be used to identify major changes in water chemistry (Fig. 9). Factor 1 has the highest factor loadings of Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-}, and EC. It accounts for 52% of the total variance. This axis reflects the role of the natural factors such as evaporate minerals dissolution of the observed high mineralization. Factor 2 is characterized by high factor loadings of HCO_3 (positive) and NO_3 (negative) and accounts for 21% of the total variance. The opposite evolution of HCO_3^{-} and NO_3^{-} could be explained by carbonate weathering and could reflect the influence of acid–base equilibrium conditions on groundwater chemistry. The high correlation between pH and bicarbonate is related to the calc-carbon balances during the dissolution of limestone and dolomite according to the process established by relations (7)–(9). This factor pits the surface water contaminated with nitrates to deep water charged with bicarbonates. These two factors indicate that groundwater in the Chemora region, is first influenced by two processes in the dissolution (carbonates and evaporates), followed by a pollution, mainly irrigation water.

Fig. 10 shows the projection of the two factor scores (*F*1 vs. *F*2) for data-sets in a 2D scatter plot. The distribution of factors scores for data-sets suggests a continuous variation of the chemical and physical properties of some of the samples. For data-sets G1, G2, and G3 are well separated in the factor space and completely consistent with the CA-derived groupings. Compact factor distributions for the majority of the water samples within the groups suggest that all the

Table 2
Rotated factor loading matrix, eigen values, % variance, and cumulative variance values

Variables	Factor-1	Factor-2
Ca	**0.96**	0.23
Mg	**0.98**	0.11
Na	**0.86**	0.14
K	**0.75**	−0.30
Cl	**0.76**	0.25
SO_4	**0.96**	0.07
HCO_3	−0.20	**0.86**
EC	**0.98**	0.22
NO_3	−0.23	**−0.82**
Eigenvalue	6.60	1.03
% Total variance	52.31	11.46
Cumulative %	52.31	73.77

Note: The bold values indicate the correlated variables.

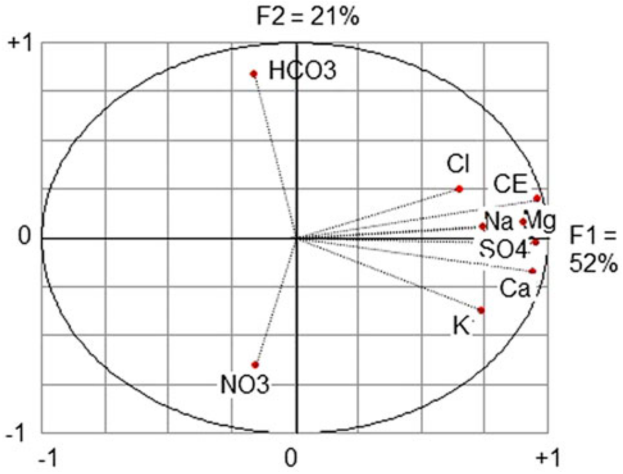

Fig. 9. Factorial plane *F*1–*F*2.

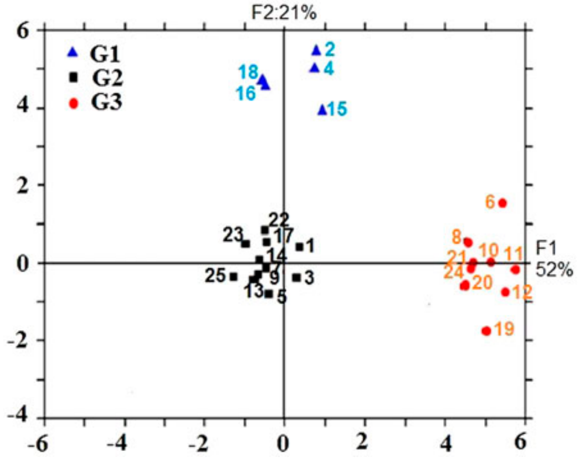

Fig. 10. Plots of PCA scores for *F*1 vs. *F*2.

water samples in their respective groups have similar chemistries and therefore similar flow paths or sources. If distribution of the samples in the factor space is broad it may indicate changes in the water chemistry due to processes such as a source of contamination, dilution, or abrupt changes in vertical–horizontal connectivity of the aquifer. Therefore, *F*1 and *F*2 are assumed to be representative of the process of acquiring the water chemistry related to the water–rock interaction and agricultural pollution.

5. Conclusion

In this study, different multivariate statistical techniques were used to evaluate variations in groundwater quality of the Chemora plain in Algeria. The groundwater hydrochemical investigation in this region helped to identify and characterize the geochemical processes of groundwater. This approach revealed that the waters are characterized by original bicarbonate facies, located on the southern and the eastern boundaries, which has gradually been replaced by dominant sulfate facies; magnesium to calcium. Environmental enrichment in calcium, magnesium, and sulfates is largely related to the alteration of pyrite in the nearby salt lake and the water concentration along the flow axis. Calculation of the SI showed that groundwater becomes saturated with calcite and dolomite at a pH 6.9 and that changes proportionally with the respective carbonates alkalinity produced by environment. Therefore, three major water facies are suggested by the Q-mode CA analysis. The samples from the Chemora area were classified as less saline water G1 with low salinity (EC < 2,500 μS cm^{-1}), G3 with high salinity (EC > 3,500 μS cm^{-1}), and G2 with intermediate salinity (2,500 < CE < 3,500 μS cm^{-1}). For the PCA, the two factors (*F*1 and *F*2) explain 73% of the total variance their loadings allow the interpretation of hydrochemical processes that could occur in the area. The results of this investigation clearly demonstrate the usefulness of the multivariate statistical analysis in the hydrochemical studies.

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