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# Origin of groundwater salinity in the Morsott-El Aouinet basin, Northeastern Algeria: hydrochemical and environmental isotopes approaches

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#### ABSTRACT

Due to its history, recharge–discharge mechanisms, geologic formations and the hydrodynamic characteristics, the groundwater of the Morsott-El Aouinet basin show a very wide range of chemistries. In this paper the groundwater hydrochemistry is studied through sampling from wells in the studied area. Hydrochemical members are identified and the sources of water salinization are defined. It was found that the evaporate within the Triassic rocks are the main contributors to the salinization of groundwater. The ionic speciation and mineral dissolution/ precipitation was calculated by WATEQF software. The increase in salinity is related to the dissolution and/or precipitation processes during the water–rock interaction and to the cationic exchange reactions between groundwater and clay minerals. The isotopic analysis of some groundwater samples shows a similarity with the meteoric waters and indicates no significant isotopic modifications by evaporation, which means that the recharge of the aquifer is quite rapid and the residence time of meteoric water in the soil zone is short.

Keywords: Triassic; Groundwater; Salinity; Environmental isotopes; Morsott-El Aouinet; Algeria

# 1. Introduction

The studied area is located within the arid zones of Algeria, situated to the north of Tebessa city and is characterised by a precipitation of less than 400 mm/y and the infiltration has been estimated at about 60 mm/y.

Its geographic boundaries are El Aouinet in the north, Morsott in the south and Meskiana basin in the west. The surface of the studied area is about 180 km<sup>2</sup> (Fig. 1).

Groundwaters play a dominant role in this part of Algeria. Because of the lack of permanent surface water

reservoirs owing to the hard climatic conditions, it constitutes the most widely available source of fresh water. In this region, groundwaters are used for domestic, agricultural and industrial purposes. Overexploitation of this resource causes a drop in the piezometric level and a progressive degradation of the water quality in the irrigated area with the occurrence of high salinity zones (EC > 23,000  $\mu$ S cm<sup>-1</sup>) which create problems of water use. The present investigation concerns the whole Morsott-El Aouinet basin. The main objectives are the hydrochemical characterisation through a study of the spatial and temporal physico-chemical distribution (Table 1) and the reconstruction of the origin and recharge mechanisms of groundwaters.

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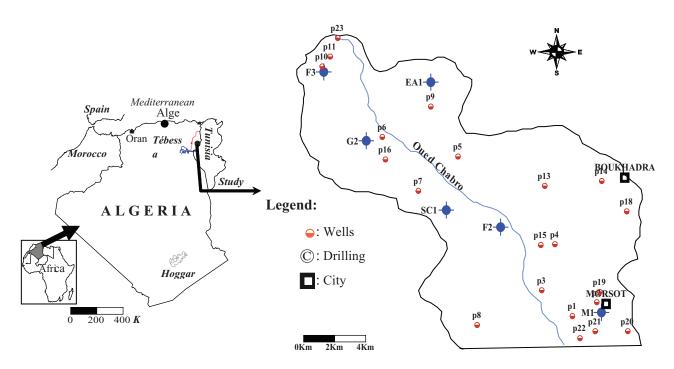


Fig. 1. Location of the study area.

Table 1
Chemical composition (in mg l <sup>-1</sup> ) of groundwater from Morsott-El Aouinet Plio-Quaternary aquifer

Wells	<i>T</i> (°C)	pН	EC (µS/cm)	$NO_3^-$	HCO <sub>3</sub>	$\mathrm{SO_4}^{2-}$	Cl <sup>-</sup>	Na <sup>+</sup>	$K^+$	$Mg^{2+}$	Ca <sup>2+</sup>	Sr <sup>2+</sup>
1	20.6	7.3	2,060	5	310.08	575	326.6	201.3	20.7	105.34	180.72	1.17
2	21.6	7.25	1,767	4.5	348.64	353	135	89.5	18.73	92.19	177.92	0.74
3	21.5	6.8	3,150	2.4	317.2	293	277.2	124.3	19.53	83.38	165.33	0.916
4	21.5	7.29	4,200	2.2	362.07	283	318.46	165.3	17.43	97.6	139.55	0.773
5	21.5	6.84	23,800	3.2	424.16	525	8144.8	3988	140.62	263.9	418.2	9.27
6	21.4	7.12	10,300	3.5	418.96	368	2130	812	41.6	294.55	387.09	4.6
8	21.4	7.5	3,510	1.2	327.4	419	809.4	399.4	27.6	132.7	231.1	3.573
7	21.3	6.75	4,650	4.5	316.07	575	355	189.2	21.34	118.6	225.03	0.9
9	21.4	7.8	1,320	2	317.62	155.61	248.5	137.34	9.91	64.7	116.52	0.689
10	21.5	7.38	7,300	5.6	288.2	280	2397	1025	78.6	204.31	269.23	3.87
11	21.3	7.42	6,800	7.2	384.2	358	2184.61	917	42.5	252.1	289.4	3.08
13	21.2	6.87	2,150	5.2	457.03	167.8	248.5	150.5	17.94	86.82	174.3	1.52
14	20.9	7.27	10,000	7.5	238.04	225	4247.86	1315.76	98.03	282	366.75	5.2
15	21.4	7.2	1,562	12.2	390.4	101.06	149.1	103.7	5.74	60.2	132.5	1.53
16	21.4	7.35	12,780	1.7	227.04	481.2	3479	1054.24	83.1	291.63	395.54	4.695
17	21.3	7.48	3,300	2.5	415	265	397.5	220.1	20.46	88.8	157.1	1.94
18	21.3	7.58	6,370	3.6	348.2	389	1150.2	402	37.52	198.5	247.4	2.13
19	21.5	7.3	1,325	9.2	302.56	136.04	127.8	91.95	7.4	62.55	113.7	1.1
20	21.3	7.35	2,120	2.7	323.6	222	248.5	163.2	9.52	81.9	156.2	1.503
21	21.1	7.6	1,359	8.1	378.7	164	198.8	109.7	10.87	92.7	146.45	1.006
22	20.6	7.34	1,154	4.2	305.44	48.66	113.6	58.7	7.01	89.5	186.2	0.539
23	21.0	7.2	1,305	4	317	140	167	101.2	7.58	62.1	117.9	1.04
24	21.3	7.3	1,450	3.1	323	135	205	139.1	13.6	42.5	107.2	1.125
25	21.4	7.4	2,110	4.21	351	82.5	411	162	10.57	85.3	117.4	0.9
26	21.4	7.25	2,320	5.93	418	222	410	258.2	18.85	90.8	141.8	1.232

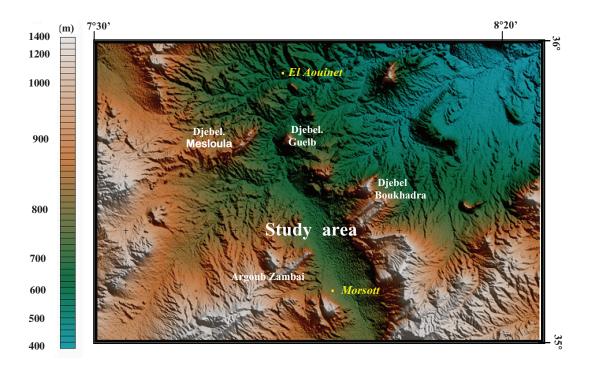


Fig. 2. Topographic map of the study area.

In addition, thermodynamic calculations were also employed, with the result that the hydrochemical evolutions of Plio-Quaternary aquifer groundwaters are not only controlled by the chemistry of the recharge water (precipitation), but also by water–rock interaction and by the mixing of fresh and saline water.

#### 2. Description of the study area

The study area is a part of a narrow trough which forms a small portion of the great Plio-Quaternary tectonic depression of Morsott (Fig. 2).

Annual precipitation in the study area ranges between 350 and 400 mm, and thus the area is considered to be a semi-arid area. Temperature can rise in the summer to 45°C. This situation of dryness accentuates the drop of the overall piezometric level especially during the last decade because the renewal of this resource is very weak.

The results of a statistical survey of the aquifer's hydraulic head and the meteorological records in the study area indicate a decrease in the average precipitation over the past 20 y and general lowering of the aquifer level by some 70 mm/y over the past 30 y [17].

## 3. Geological and hydrogeological setting

The local geology was studied by several authors [3,4,21]. The micropaleontologic and biostratigraphic

analysis, has showed that from the stratigraphic point of view, the study area covers the Plio-Quaternary tectonic basin of Morsott. This depression separates the diapir of Argoub Zamabai situated in the West from the one of Boukhadra in the East (Fig. 2).

The study area is constitued in the major part by cretaceous formations (Fig. 3), forming a succession of anticlines and synclines. The stratigraphic sequence is presented in the form of alternation of carbonated formations of limestones, marly-limestones and argillaceous marls.

The Plio-Quaternary and quaternary terrains occupy the central part; they are consisted by actual and recent alluvial deposits, conglomerates, gravels, sandstones, etc.

The summary analysis of the stratigraphic column of the study area shows the presence of three aquiferous formations which are the Eocene limestone aquifer, the Maestrichtian limestone aquifer and Plio-Quaternary aquifer (Fig. 4), this last one is a free aquifer of great extension occupies the major part of the tectonic basin, limited at the West and at the East by two great faults of NW-SE orientation which isolate the deeper aquifers. It is constituted by very varied deposits such as, alluvial fans, silts, calcareous crust, conglomerates and gravels. This aquifer plays a great role in the drinking water supply of the inhabitants of this area.

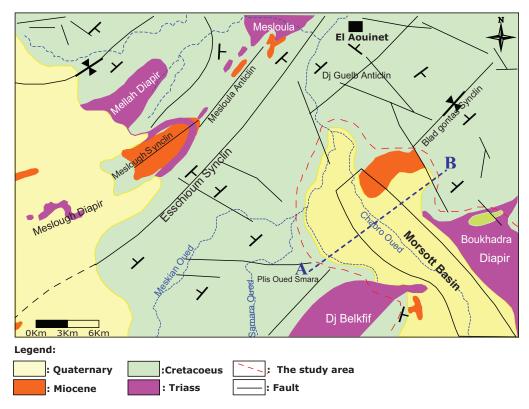
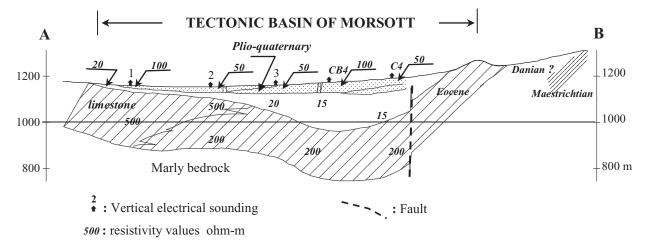


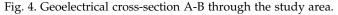
Fig. 3. Geological map of the study area.

## 3.1. Sampling and analysis

Groundwater samples were collected for geochemical analysis at different depths from 26 production wells penetrating the shallow aquifers (Fig. 5).

Eight groundwater samples from study area wells were taken for isotopic analysis (Table 4). The groundwater samples were distributed uniformly throughout the study area. The stable isotopes analyses were performed in the Jordanian Water Authority labs by using a Finnigan-Matt 251 ratio mass spectrometer. For hydrogen, samples were reacted at 750°C with Cr metal using a Finnigan H/device coupled to the mass spectrometer. For oxygen, samples were equilibrated with CO<sub>2</sub> gas at approximately 15°C in an automated equilibration device coupled to the mass spectrometer. Standardization is based on international reference materials VSMOW (Vienna standard mean ocean water).





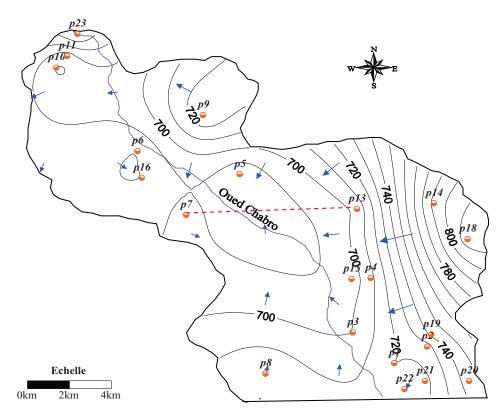


Fig. 5. Piezomeric map of the study area. Mar-Apr. 2006.

#### 4. Results and discussion

Chemical data are presented in Table 1. The following discussion will illustrate the significance of these results in the context of groundwater movement, water types, water–rock interactions and origin of salinity.

## 4.1. Groundwater movement

The groundwater flow system of the Plio-Quaternary aquifer is presented as a groundwater contour map. Two piezometric highs are recognized in the study area. One has a static water level of 800 m and is located in the south east. The second is in the north-west of the study area and has a static water level of 690 m.

The groundwater flow is shown on the piezometric map in Fig. 5. Generally, the groundwater flow direction in the study area is converging in the centre towards Chabro wadi.

# 4.2. Classification of the water

A lot of classification methods have been developed to differentiate freshwater from saltwater and to define the degree of salinity of the water [8,20,2]. Salinity is the total amount of inorganic solid materials dissolved in any natural water and is normally expressed in terms of total dissolved solids (TDS).

These somewhat arbitrary classifications of freshwater, brackish water and brines are based on the suitability of the water for human consumption and usage.

Table 2 shows the water classes according to the classification of [8].

Groundwater samples were plotted in a  $Cl^-$  vs.  $Ca^{2+}$  and  $Mg^{2+}$  diagram to show the different water types in the study area as shown in Fig. 6.

However, the different water samples have been classified according to their chemical composition using the Piper diagram [15,19].

The Piper diagram (Fig. 7) shows that the overall chemical character falls within the following water types:

- A fresh groundwater end-member: Ca–HCO<sub>3</sub> water type with low salinity concentrations.
- A saline water end-member: predominantly Na–Cl water type with high salinity concentrations.

The first water type changed continuously due to the influence of many factors.

Firstly, the water–rock interaction between groundwater and aquifer materials and secondly, the influences

Table 2	
Mean average values of the calculated parameters	

Parameter	Minimum	Maximum	Mean	$S.D^*$
$\log pCO_2$	-2.362	-1.276	-1.811	0.284
CO <sub>2</sub> total	0.00396	0.00937	0.00648	0.00143
Ionic strength	0.0183	0.257	0.0625	0.0499
Total Alcalinity	3.74	7.50	5.81	1.132
SI Anhydrite	-1.889	-0.955	-1.35	0.2423
SI Aragonite	-0.317	0.666	0.214	0.2465
SI Brucite	-5.941	-3.953	-4.83	0.528
SI Calcite	-0.171	0.812	0.359	0.2466
SI Celestite	-2.138	-0.959	-1.516	0.385
SI Dolomite	-0.314	1.858	0.851	0.52
SI Gypsum	-1.681	-0.716	-1.116	0.246
SI Halite	-6.545	-3.26	-5.381	0.865
SI Magnesite	-0.505	0.684	0.127	0.279
pH equilibrium	6.75	7.8	7.26	0.353

S.D\*: standard deviation.

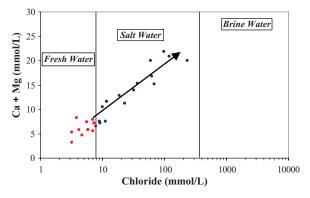


Fig. 6. Cl vs. Ca and Mg in mmol/L for groundwater samples [22] in red color : wells P1, P3, P8, P15, P19, P20, P21, P22, P23, P24, P25. In blue color: the rest of the wells.

of human activities such as irrigation return flow and overexploitation of the aquifer system. The result is indicated by a rapid increase in sodium, sulphate and chloride concentrations in the aquifer.

By following the direction of groundwater flow, the water changes its chemistry and becomes more saline, whereby the high sodium concentration is usually an indication of cation-exchange process.

# 4.3. Hydrogeochemical analysis of the salinization process within the Plio-Quaternary aquifer

During sampling, Plio-Quaternary aquifer waters shows a chemical type dominated by a Na–Cl water with high salinity concentrations (between 1,200 and 13,300 mg/L), electric conductivity is generally high, oscillating between 1,154 and 23,800  $\mu$ S/cm with an average of 5214.8  $\mu$ S/cm (Table 1).

The zones of high mineralization are localised in the east and the north parts of the study area, however the low values of mineralization are localised in the south part.

In the east part (Djebel Boukhadra), centre and north part (Djebel Belkfik and Djebel Mesloula), the influence of the saline triassic formations rich in halite is a sighted (Fig. 8). We noticed an increase in the total mineralization at the well no. 5 reaching a TDS value of 13,000 mg/l.

In the south of the study area (region of Morsott), the influence of triassic formations decreases and the total mineralization varies between 1,100 and 2,100 mg/l, the chemical facies becomes  $Ca-HCO_3$  and  $Ca-SO_4$  water types, with low salinity concentrations, indicating the influence of the carbonated formations and those of marly formations of Cenomanian and Turonian (rich in gypsum).

On the basis of the differentiation, analysis of the behaviour of certain ions was undertaken using chloride ion, which is considered to be a conservative tracer of the salt water intrusion process from saline triassic formations. The samples are presented in different diagrams in respect to the binary line of mixing fresh and saline water, which are calculated and presented in Fig. 9.

The groundwater samples of different wells show in general enrichment in  $Ca^{2+}$  and poverty in  $Na^+$ ,  $K^+$  and  $SO_4{}^{2-}$ , while for the  $Mg^{2+}$  there is a dispersion of the points around line of mixture. The major reactions recognized responsible for the enrichment or impoverishment of the chemical elements in groundwater are the  $Ca^{2+}$ – $Mg^{2+}$  exchange due to the interaction carbonated water–rocks, the basic exchange  $Na^+$ – $Ca^{2+}$ 

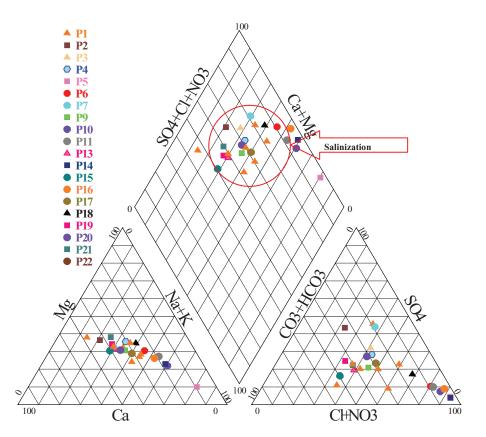


Fig. 7. Piper trilinear diagram of water chemistry in the study area.

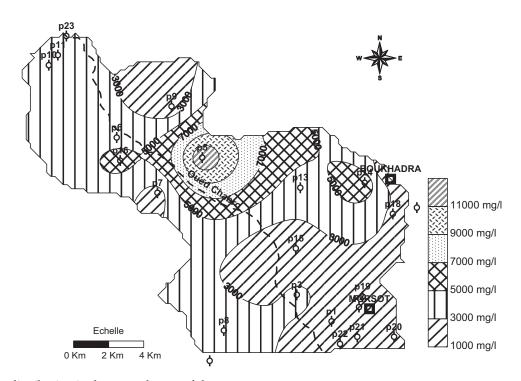


Fig. 8. Salinity distribution in the groundwater of the area.

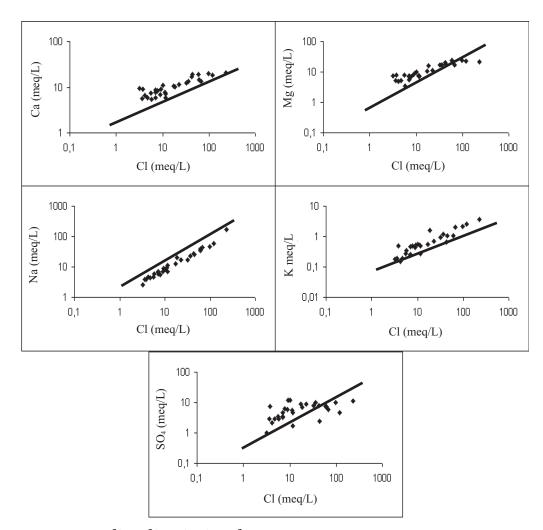


Fig. 9. Relationship between  $Ca^{2+}$ ,  $Mg^{2+}$ ,  $Na^+$ ,  $K^+$ ,  $SO_4^{2-}$  and  $Cl^-$ .

or  $Na^+$ – $Mg^{2+}$  and the reduction or the dissolution of sulphates [10].

The relation between  $Mg^{2+}$  and  $Cl^{-}$  shows an enrichment of almost 50% of the analysed water samples compared to the mixture line. This enrichment can be due to the dissolution of dolomite.

The relation between  $SO_4^{2-}$  and  $Cl^-$  shows that the major groundwater samples are plotted on the mixing line of fresh and saline water except for some points which are under this line. The sulphate enrichment is related to the dissolution process of triassic outcrops and within the aquifer beds which contains sulphate bearing minerals such as gypsum and anhydrite and/or to a contamination of agricultural origin.

The graph  $Na^+$  vs.  $Cl^-$  shows that all the groundwater samples are plotted under the mixing line of fresh and saline water. The  $Na^+$  deficit is explained by the basic ionic exchange phenomenon between water and the aquifer; which led to a  $Na^+$  adsorption by clayey phase and a release of  $Ca^{2+}$ . The relation between  $K^+$  and  $Cl^-$  indicates that most of the groundwater samples are plotted on the mixing line which indicates enrichment by triassic outcrop dissolution and/or an anthropogenic source in respect of the agricultural fertilizers [18].

For a more in-depth characterisation of salinization processes in the Plio-Quaternary aquifer from the study area, estimation of the percentages of each ion in respect of the total ions was carried out by using a Chebotarev diagram [14], which represents the percentages of bicarbonate ions, against the summarized percentage of chloride, sulphate and nitrate in respect of mixing between the fresh and saline water components.

When sodium-bearing clay interacts with a solution in which calcium is the predominant ion, each couple of solubilized sodium ions are replaced by one absorbed calcium, while sodium is tending toward saturation or equilibrium [14]. This type of reaction is known as direct exchange and is responsible for certain

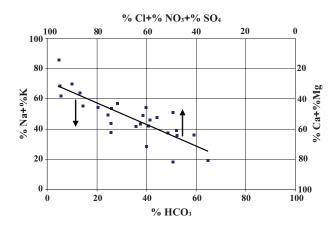


Fig. 10. Chebotarev diagram represents hypothetical line of mixing between fresh and saline water in the study area ( $\uparrow$  direct ionic exchange;  $\downarrow$  inverse ionic exchange).

anomalies of both sodium and calcium ions with respect to the binary mixing of fresh and saline waters [1]. In some cases, the direction of exchange reactions appears to be anomalous, i.e. when calcium is adsorbed into the clayey phase; it is given up to solution in exchange for dissolved sodium. This type of reaction is known as inverse exchange [14]. From the above considerations, the main hydrochemical features of the Plio-Quaternary aquifer are be defined as follows:

- The water in the region of Morsott (in the south of the study area) constitutes a separate chemical group. The fresh water generally has an excess of Ca<sup>2+</sup> accompanied by a deficit in Na<sup>+</sup>. This situation can be attributed to a process of inverse exchange.
- The saline water from the rest of the aquifer (i.e., Boukhadra and Mesloula areas) reflects an increase in Na<sup>+</sup>, which corresponded to deficits in Ca<sup>2+</sup>, a situation, which is related to direct ion exchange.

The Chebotarev diagram (Fig. 10) is interpreted by the mentioned hydrochemical composition. The deviations with respect to the mixing line should be interpreted as effects of the modifying process primarily in respect of the cation contents.

Ideally, the samples affected by the mixing of salt waters should follow the mixing line, but vertical displacements of positions as shown in the diagram are due to both direct and inverse ionic exchange processes controlling the cation contents.

#### 4.4. Water–rock interaction process

Interactions between groundwater and surrounding host rocks are believed to be the main processes responsible for the observed chemical characteristics of groundwaters in the Morsott-El Aouinet Plio-Quaternary aquifer. Evaluation of such processes requires the description of the mean mineral assemblage of the rocks in which water is found, and the identification of chemical reactions responsible for the geochemical evolution of groundwaters. From available studies in the literature, such reactions generally include chemical weathering of rock-forming minerals, dissolution–precipitation of secondary carbonates and ion exchange between water and clay minerals [7].

Two approaches, mathematical and graphical, are generally used for the resolution of hydrogeochemical problems. The mathematical approach is often used for the calculation of saturation indices with respect to mineral phases, thus providing some indication upon the equilibrium state between groundwater and surrounding minerals rock assemblage [17].

In this present paper, different parameters calculated based on the chemical analyses of the water samples include pH-equilibrium,  $pCO_2$ , ionic strength and saturation indices for calcite, dolomite, gypsum, anhydrite, magnesite, celestite, barite, siderite and halite.

Saturation indices express the extent of chemical equilibrium between water and mineral phases in the matrix of the aquifers and could be regarded as a measure of dissolution and/or precipitation processes relating to the water–rock interaction [9].

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

$$SI = \log(K_{iap}/K_{sp}) \tag{1}$$

where  $K_{iap}$  is the ionic activity product of the ions,  $K_{sp}$  is the solubility product of the mineral, and SI is the saturation index.

- If SI < 0: The water is undersaturated with respect to a certain mineral which means that the water is still able to dissolve that specific mineral.
- If SI > 0: The water is oversaturated with respect to that mineral and the mineral will precipitate.
- If SI = 0: Water is in equilibrium.

WATEQF [16] is used to calculate the ionic speciation of the waters, the ionic activities, the theoretical  $pCO_2$  and most importantly, the saturation indices of calcite, aragonite, dolomite, gypsum, anhydrite, halite, celestite and brucite.

The significant results are that all the groundwater samples listed in Table 3, were found to be saturated with respect to calcite, dolomite, aragonite and magnesite but undersaturated with respect to halite, gypsum, anhydrite, celestite and brucite.

Table 3 Groundwater classification using total dissolved solids Davis and DeWiest [8]

Class	TDS (mg/L)
Fresh	0–1,000
Brackish	1,000–10,000
Saline	10,000-100,000
Brine	>100,000

Fig. 11 shows the distribution of the computed  $pCO_2$  values (on a log scale) for all the considered groundwater samples. These computed values vary between  $10^{-2.8}$  and  $10^{-1.0}$  atm, being significantly higher than that of the atmosphere  $pCO_2$  ( $10^{-3.5}$  atm). Such elevated values suggest that the groundwater system is open to soil CO<sub>2</sub>. The source of dissolved CO<sub>2</sub> can be determined on the basis of <sup>13</sup>C analyses (anthropogenic or biogenic origin).

The ionic activity products for the calcite solubility equilibrium and the solubility products equation for gypsum (Fig. 12), show samples which have values greater than the equilibrium constant are supersaturated only with respect to calcite.

Fig. 13 shows the plots of all the investigated groundwaters, in both Na<sub>2</sub>O–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>-H<sub>2</sub>O (Fig. 13(a)) and  $K_2O$ –Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–H<sub>2</sub>O (Fig. 13(b)) partial systems. In both diagrams, almost all the groundwater samples plot in the stability field of kaolinite and gibbsite which may be the main clay minerals in which these groundwaters were found.

The above observations suggest that groundwater samples of the study area are contained in a mineral environment mainly made up of aluminosilicates. It is therefore possible that the chemical composition of this group of groundwaters may be attributed to equilibrium between primary aluminosilicate minerals and kaolinite and also between kaolinite and gibbsite, as

Table 4 Isotopic composition of groundwater from the Plio-Ouaternary aguifer

Quiternary uquiter						
Samples	Wells	Altitudes (m)	$\delta H^2$	$\delta O^{18}$		
1	2	725.2	-38.5	-7.18		
2	5	681.6	-33.2	-6.64		
3	7	709.0	-34.9	-6.63		
4	9	730.0	-35.6	-6.82		
5	10	701.0	-32.3	-6.2		
6	1	721.4	-39.4	-7.1		
7	6	680	-32.4	-6.22		
8	16	701.5	-32.8	-6.4		

spheric Pressure -3.5 -3 log pCO<sub>2</sub> (atm) -2.5 -2 -1.5 \_1 -0.5 à 210 Ì ひてくてん 20 2 ళిపై సై స్ట్రో à Wells

Fig. 11. Distribution of equilibrium partial pressure of CO<sub>2</sub> (on log scale) as computed with WATEQF.

described by the following reaction equations for example:

$$2albite + 11H_2O + 2CO_2 = kaolinite + 2Na + + 2HCO_3^- + 4H_4SiO_4$$
(1)

$$\begin{array}{ll} 0.5Al_2Si_2O_5(OH)_4 + 2.5H_2O &= Al(OH)_3 + H_4SiO_4 \\ \text{kaolinite} & \text{gibbsite} \end{array} \tag{2}$$

This process generally enriches the groundwater in rock-forming elements such as  $Na^+$ ,  $Ca^{2+}$ ,  $K^+$  and dissolved SiO<sub>2</sub> and results in the formation of Ca–Na–HCO<sub>3</sub> type groundwater. Carbon dioxide of biogenic origin is among the key factors that governs the above reaction [20].

The observed heterogeneity in  $Ca^{2+}$  and  $Na^{+}$  concentrations for these groundwater samples may reflect local mineralogical changes in the groundwater reservoir and/or variations in the weathering rate with regard to the production rate of carbon dioxide.

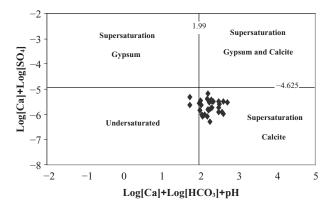


Fig. 12. Calcite and gypsum equilibrium solubility relationship, 25°C and 1 atm pressure for the analysed groundwater samples.

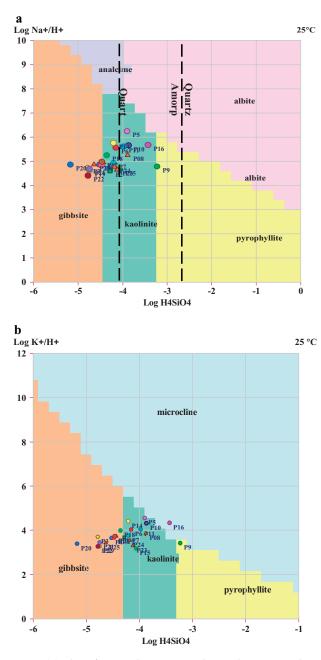


Fig. 13. (a) Plot of groundwater samples in the  $Na_2O-Al_2O_3-SiO_2-H_2O$  system at 25°C and 1 atm. (b) Plot of groundwater samples in the  $K_2O-Al_2O_3-SiO_2-H_2O$  system at 25°C and 1 atm.

#### 5. Origin and recharge mechanisms of groundwaters

The use of stable isotopes is very important in the field of evaluation of the resources, [11–13]. Stable isotopes of oxygen and hydrogen in groundwater of an active hydrological cycle derive from and reflect the initial isotopic composition of the recharging rainwater. Within the coordinate system of  $\delta^{18}$ O and

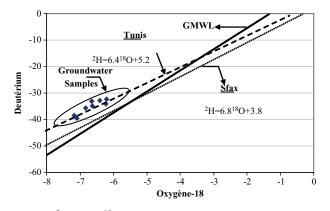


Fig. 14.  $\delta^2 H$  vs.  $\delta^{18} O$  relationship for groundwater in the study area.

 $\delta^2$ H it is possible to discern a meteoric line, the slope of which is characteristic of a certain hydrological system [13].

In this paper the  $\delta^{18}$ O and  $\delta^2$ H values of precipitation samples, used to establish the local meteoric water lines, are obtained from the Global Network for Isotopes in Precipitation database managed by the AIEA, for a period of 6 y (September 1992–December 1998) for Tunis–Carthage and Sfax meteorological stations (Tunisia).

The meteoric water lines defined for Sfax and Tunis (Fig. 14) have been calculated using a least squares regression [5]:

$$\delta^{2}H = (6.4 \pm 0.5)\delta^{18}O + (5.2 \pm 1.7);$$
  
Tunis (1992 - 1998, *n* = 26)

$$\delta^{2}H = (6.7 \pm 0.3)\delta^{18}O + (3.5 \pm 1.3);$$
  
Sfax (1992 - 1998,  $n = 45$ )

The water lines of Tunis and Sfax for the period 1992–1998 are close and thus seem to be representative of the precipitation isotopic content in Tunisia. The comparison between the Tunisia and the Global Meteoric Water line [6] shows evidence of the evaporation that affects Tunisian precipitation as the rain falls.

#### 5.1. Groundwater isotopic signatures

Stable isotope compositions of water from the Plio-Quaternary aquifer are presented in Table 4. These data show that the number of wells analysed for oxygen-18 is relatively restricted and not representative for the whole aquifer. Stable isotope values were found to vary between -7.18 and -6.2 in <sup>18</sup>O with a mean of  $-6.65 \pm 0.2 \%$  (n = 8) and from -39.4 to -32.3 in <sup>2</sup>H with a mean of  $-34.88 \pm 00 \%$  (n = 8).

The oxygen and deuterium contents for all the investigated groundwaters are plotted in the classical  $O^{18}$ –H<sup>2</sup> diagram (Fig. 14), together with the so-called global meteoric water line (d H<sup>2</sup>=8 ¥ d O<sup>18</sup>+10), defined by Craig (1961) and the local meteoric water lines (Tunis and Sfax). The plot of data points in such diagram provides some indication upon the origin and the recharge processes of groundwaters. Fig. 14 shows that the groundwater samples are distributed around the Tunis meteoric line, and indicates no significant isotopic modifications by evaporation, which means that the recharge of the aquifer is quite rapid and residence time of meteoric water in the soil zone is short

#### 6. Conclusion

The groundwater quality can be described as bad on the whole of the study area, except for some samples.

A high concentration of elements like chlorides, sodium, sulphate, etc. constitutes a visual harmful effect and can make necessary the water treatment.

A problem of salinity was recognized in almost all the study area due to the influence of triassic formations rich in halites (Boukhadra and Masloula diapers).

The cartographic representations of the different geochemical parameters show that the natural qualities of groundwaters vary according to the geological and hydrogeological contexts and also allowed us to locate the anomalies of salinity.

The ionic speciation and mineral dissolution/precipitation was calculated by WATEQF package software. The increase in salinity is related to the dissolution and/or precipitation processes during the water–rock interaction and to the cationic exchange between sodium and calcium.

The isotopic analysis of some groundwater samples shows a similarity with the meteoric waters reflect their short residence time and a lowest evaporation phenomenon of infiltrated groundwater.

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