



Hydrochemical and isotopic assessment of groundwater quality in the Quaternary shallow aquifer, Tazoghrane region, north-eastern Tunisia



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ABSTRACT

The major ion hydrochemistry and environmental isotope composition (^{18}O , ^2H) of the Tazoghrane shallow groundwaters were investigated to identify the sources and processes that affect the groundwater composition. The Quaternary shallow aquifer of Tazoghrane represents one of the most important aquifers in the Cap Bon peninsula. Groundwater from this aquifer is classified into two water types: $\text{Ca}-\text{SO}_4-\text{Cl}$ and $\text{Na}-\text{Cl}$. The groundwater composition is largely controlled by the water–rock interaction, particularly the dissolution of evaporate minerals and the ion exchange process. Elevated content of nitrates indicates that agricultural activities are probably the most significant anthropogenic sources of nitrogen contamination. The stable isotopic signatures reveal two water groups. Non-evaporated waters, which are distinguished by depleted d^{18}O and d^2H contents, indicate the significant recharge by modern rainfall from Mediterranean air masses. Evaporated waters that are characterized by relatively enriched d^{18}O and d^2H contents indicate an important component of recharge by return flow of irrigation waters.

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1. Introduction

The Tazoghrane region, which covers a total area of about 250 km^2 , represents one of the most important agricultural districts in the Cap Bon peninsula, north-eastern Tunisia (Fig. 1). It is characterized by a semi-arid, "Mediterranean" climate with mild, wet winters and warm, dry summers. Under pressures of population, climate change, and pollution, the Tazoghrane region faces substantial challenges in the management of scarce freshwater resources. During the last two decades, the shallow aquifer groundwater has been over-exploited through excessive, uncontrolled pumping mainly for domestic and agricultural purposes. Unplanned and substantial withdrawals of groundwater from the Tazoghrane shallow aquifer for irrigation purposes have resulted in severe water level decline of up to 5 m in some areas (DGR, 2005) and groundwater quality degradation induced by the soil leaching and fertilizer transfer to groundwater, especially in areas with intensive agricultural activities. Management, assessment and protection of the aquifer is therefore of fundamental importance to human life and economic activity in the region. The origins of groundwater mineralization, in relation to their natural and

anthropogenic environment, were studied in several rural areas in the Cap Bon peninsula, northeastern Tunisia. The literature dealing with the qualitative aspects of groundwater treats in detail the spatial distribution of physico-chemical parameters, correlations between major elements and isotopic investigation in order to identify the main mineralisation processes (Trabelsi et al., 2005; Ben Hammouda et al., 2009; Ben Moussa et al., 2012; Charfi et al., 2013). However, none of these studies has emphasized the Tazoghrane groundwater quality degradation. The present investigation, which reports the first characterization of the Tazoghrane shallow aquifer, integrates geochemical and isotope datasets to highlight the hydrodynamic functioning of the Quaternary shallow aquifer and identify natural and anthropogenic processes that control the groundwater quality, origin and migration pathways.

2. Study area

Geologically, the Tazoghrane region is situated in the eastern part of the Tunisian Atlas. It is limited to the south and the southwest by the Dakhla syncline, Jebel Sidi Abd ar Rahman anticline, Takelsa syncline and Jebel Korbous monocline. It is affected by folding and faults in NW–SE, NE–SW and E–W directions. Sedimentary series extend from middle Miocene to Quaternary (Fig. 2). The lithological description of these sediments (Ben Salem, 1995) reveals that the

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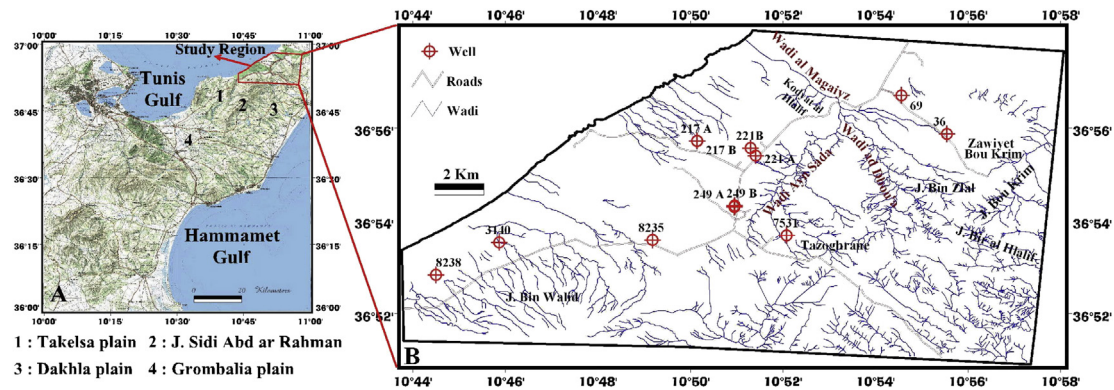


Fig. 1. A: Location map of the Tazoghrane region. B: hydrographical network map of the study area.

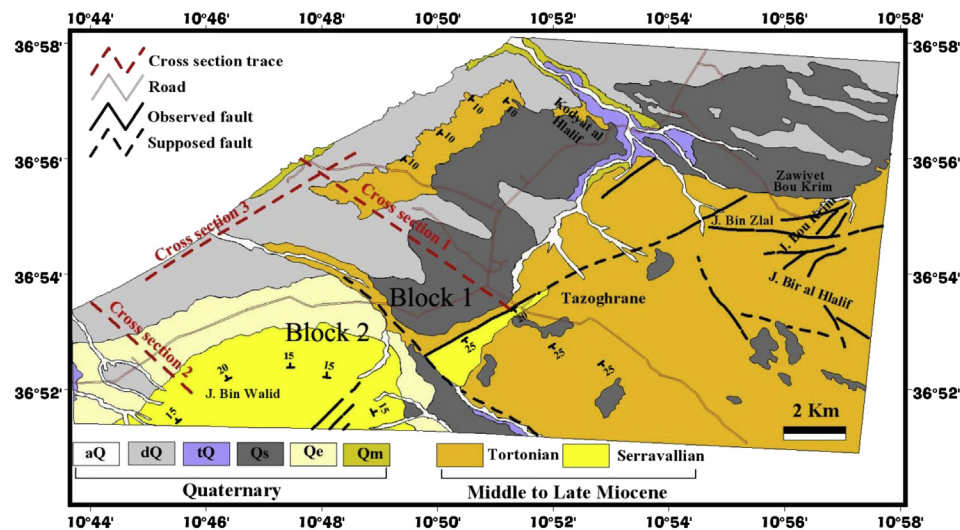


Fig. 2. Portion of the geological map of Tazoghrane region (Ben Salem, 1989).

Middle to Late Miocene is represented by the Beglia and Saouaf formations. The Beglia Formation has an average thickness of about 600 m, and consists of fine and consolidated sandstone. The Saouaf Formation of almost 1000 m thickness is composed of alternating clays with sandstone intercalation, and sandstones with clay intercalation. The Quaternary series unconformably overlies the Miocene series and is divided into six units, from bottom to the top (Fig. 3): ancient dunes (Qm) scree (Qe), soils (Qs), sands and conglomerate (tQ), recent dunes (dQ) and alluvium (aQ).

Hydrologically, the Quaternary series of about 50 m thickness hosts the shallow aquifer of the Tazoghrane region (Fig. 4). They occupy almost the half of the study region surface and fill two blocks of different geometry that are separated by a NW–SE fault (Fig. 2). The shallow aquifer, which represents the largest water producer, is tapped by several private and state owned wells with depths ranging from ~10 to 30 m.

The soils in the area have developed into a loamy material derived from marls to sandstone. Luvisols, cambisols and vertisols are cultivated annually. Regosols are more commonly associated with pasture and shrubs. The soil depth varies highly from a few cm to 200 cm. The study area is distinguished by intensive agricultural

production. These are annual cropland, such as cereals and legumes, and perennial croplands of olive, citrus, and vineyards.

3. Methods

During the sampling campaign carried out in March 2013, water samples from 12 shallow wells were collected for geochemical and isotopic analyses. Temperature ($T^{\circ}\text{C}$), pH and electrical conductivity (EC) were directly measured in situ using portable meters with temperature compensation and calibration. Total Dissolved Solids (TDS) were determined by evaporating the sample and drying it at 105°C . Chemical analysis of the water samples were carried out in the "Laboratoire de Radio-Analyses et Environnement" of the School of Engineers of Sfax, Tunisia. Major cation concentrations were measured on a Waters Ion chromatograph using IC-PakTM CM/D columns. Major anion concentrations were measured using a Metrohm ion chromatograph equipped with CI SUPER-SEP columns. The analysis of bicarbonates was undertaken by titration to the methyl orange endpoint.

Oxygen-18 and deuterium analyses were performed in the "Laboratoire de Radio-Analyses et Environnement" of the School of Engineers of Sfax, Tunisia, using the Laser Absorption Spectrometer LGR DLT 100 (Penna et al., 2010). Results are reported with V-

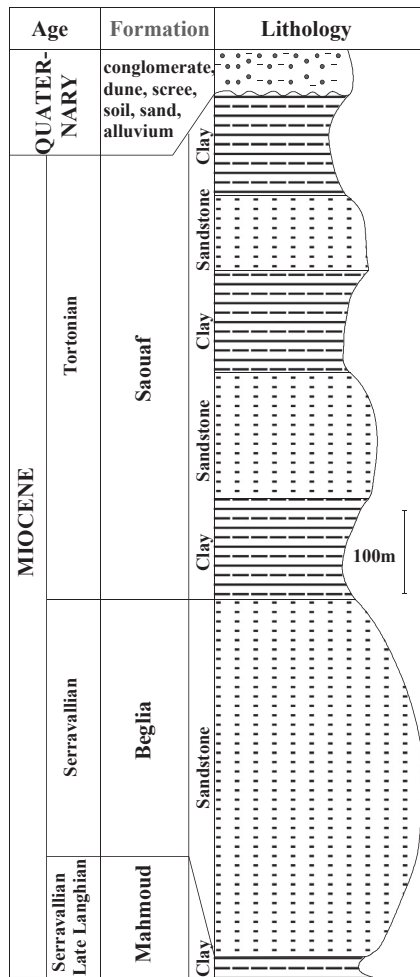


Fig. 3. Lithostratigraphic column of the study region (Errachi and Ajlani, 2013).

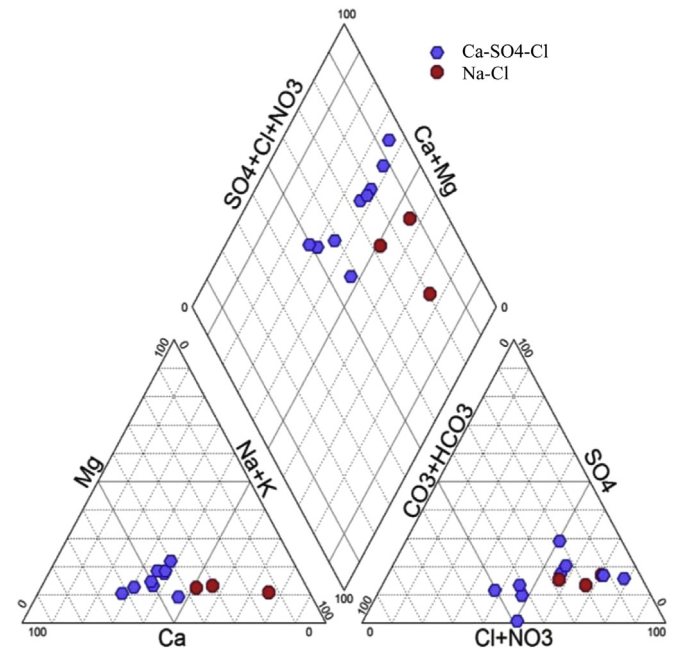


Fig. 5. Piper diagram of the shallow aquifer groundwaters.

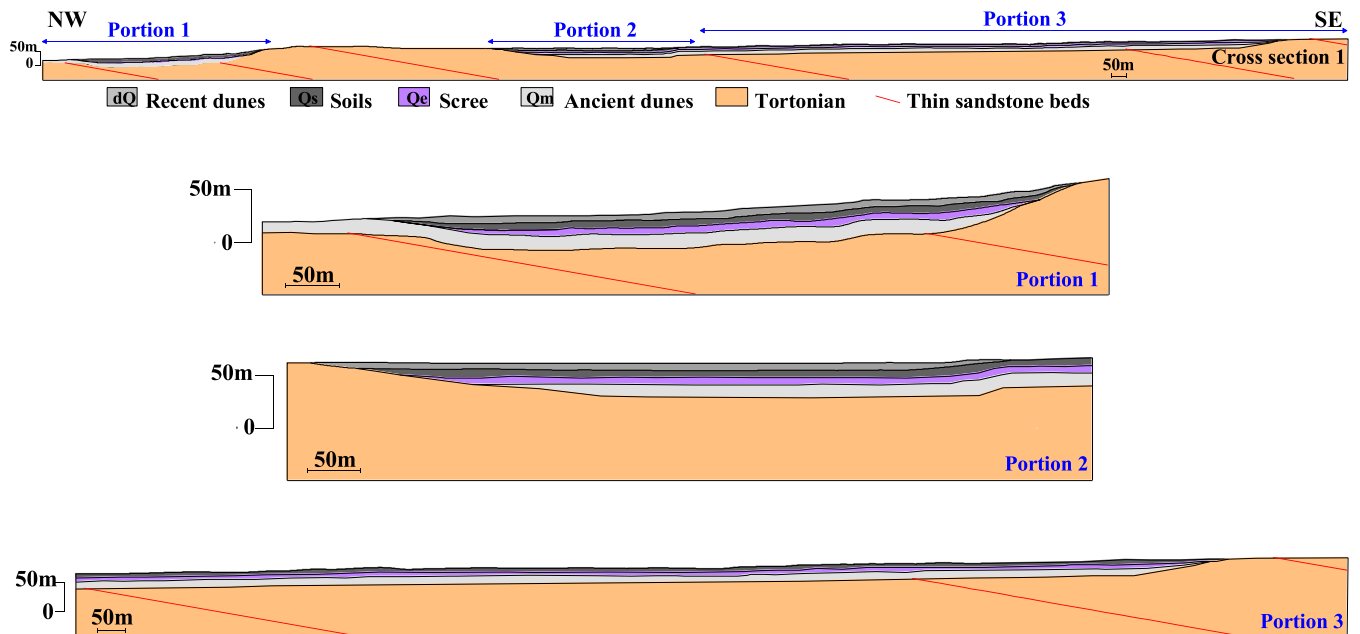


Fig. 4. NW-SE geological cross section showing the angular unconformity of the Quaternary series on the Tortonian series (Saouaf formation).

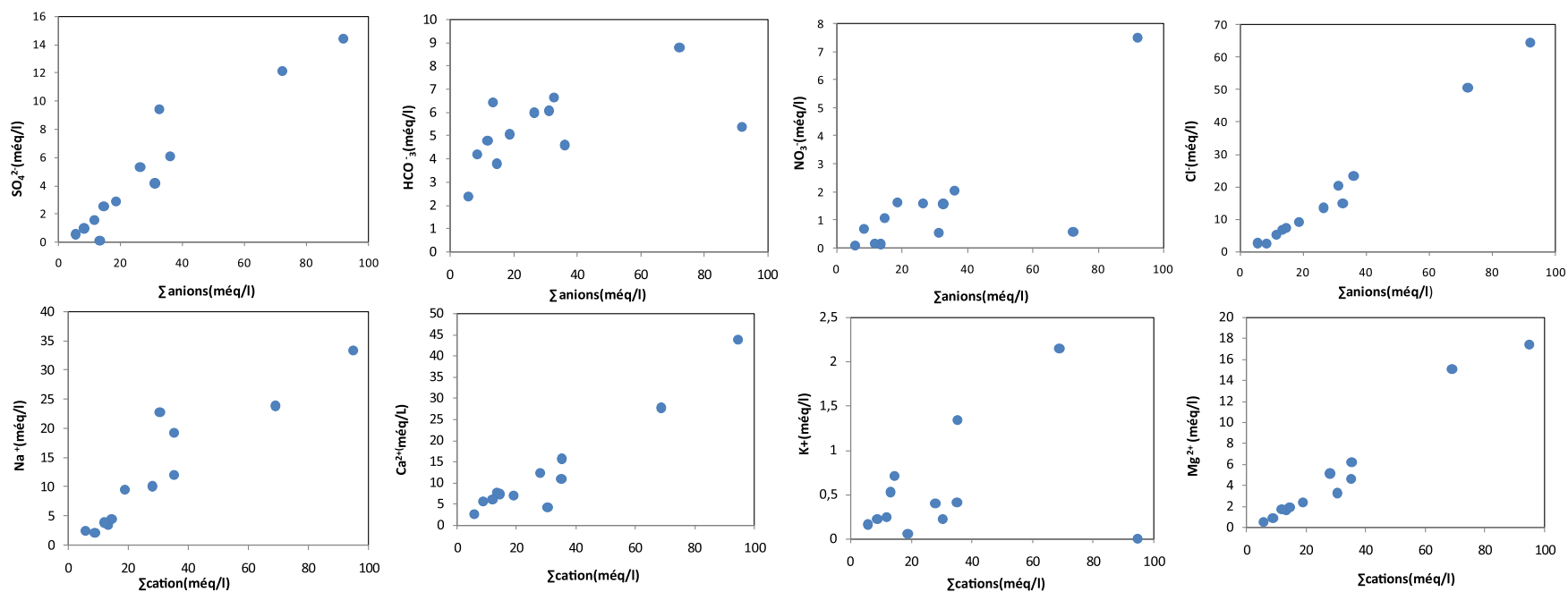


Fig. 6. Plots of Σanions versus each anion and $\Sigma \text{cations}$ versus each cation.

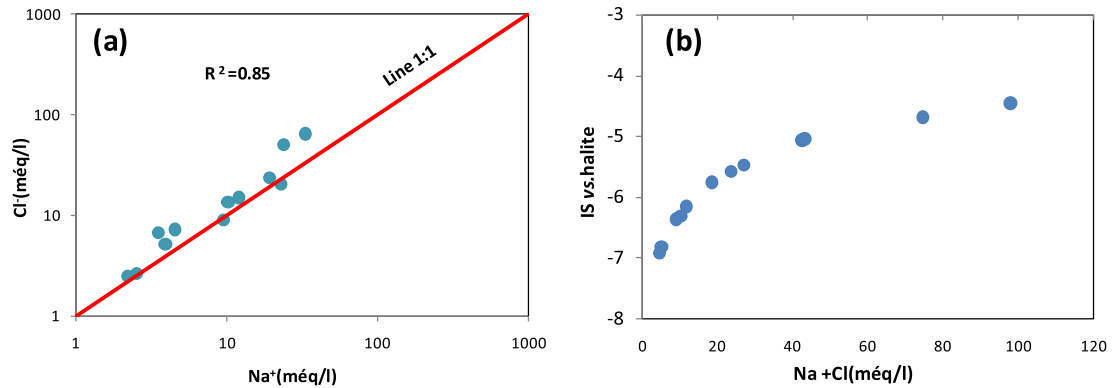


Fig. 7. Plots of Na versus Cl (a) and (Na + Cl) versus SI of halite (b); (SI = saturation index).

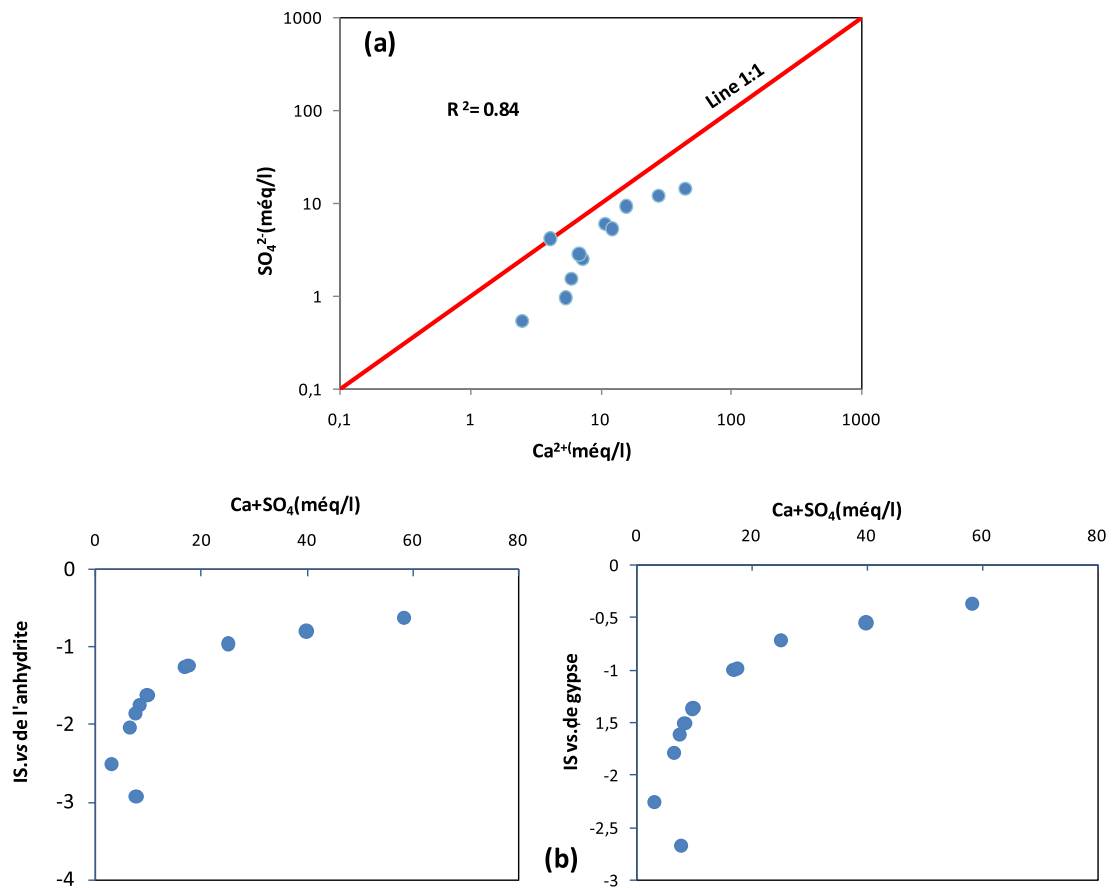


Fig. 8. Plots of Ca versus SO_4 (a), ($\text{Ca} + \text{SO}_4$) versus SI of anhydrite and ($\text{Ca} + \text{SO}_4$) versus SI of gypsum (b).

SMOW standard (Vienna-Standard Mean Ocean Water). Precision of analyses was $\pm 0.60\%$ for ^2H and $\pm 0.20\%$ for ^{18}O .

The partial pressure of carbon dioxide ($p\text{CO}_2$) was estimated by using WATEQ4 F program (Ball and Nordstrom, 1991). The Piper diagram was established to identify the different water types (Piper, 1944).

4. Results and discussion

4.1. Field parameters

Chemical characteristics of groundwater samples are presented in Table 1. The $\log(p\text{CO}_2)$ values vary

between -2.1 and -1.4 with an average of -1.7 . The highest values, which were registered mainly downstream, provide insight into the more extensive water–rock interaction and the microbial mediated reactions in relation with the relatively longer residence times (Rightmire, 1978; Adams et al., 2001). The lowest values characterize wells located upstream, reflecting the significant contribution of the recent fresh waters to the recharge of the shallow aquifer. Temperature and pH values range from 15 to 21.2°C and from 7.6 to 8.2 ms/cm, respectively. The Electrical Conductivity (EC) and the salinity values vary largely from 1.06 to 6.6 ms/cm and from 0.5 to 6.05 g/l, respectively.

Table 1

In situ measurements, geochemical and isotopic data of Tazoghrane shallow groundwater.

Well	pH	T°C	CE ms/cm	Cl	NO ₃	SO ₄	HCO ₃	Na	K	Mg	Ca	δ ² H	δ ¹⁸ O
				meq/l									% vs. SMOW
7531	7.8	21.20	2.95	14.9	1.6	9.4	6.6	12.1	1.3	6.2	15.6	−27.7	−5.0
249B	8.04	16	1.33	6.6	0.1	0.1	6.4	3.5	0.5	1.7	7.5	−23.8	−4.5
249A	8.7	15	1.32	7.2	1.1	2.5	3.8	4.5	0.7	1.9	7.2	−23.1	−4.4
217A	8.13	15.3	6.63	2.6	0.1	0.5	2.4	2.5	0.2	0.5	2.5	−29.5	−5.1
217B	8.22	16.3	8.19	64.5	7.5	14.4	5.4	33.4	0.0	17.4	43.9	−24.3	−4.6
221A	7.87	16.6	3.48	23.3	2.1	6.1	4.6	19.3	0.4	4.6	10.8	−21.4	−3.9
221B	8.04	17.4	1.7	9.0	1.6	2.9	5.1	9.6	0.1	2.4	6.9	−26.0	−4.7
69	7.96	19.4	3.24	20.4	0.5	4.2	6.1	22.8	0.2	3.3	4.1	−29.2	−5.5
36	7.81	17.1	2.49	13.5	1.6	5.3	6.0	10.2	0.4	5.1	12.2	−26.5	−4.9
8235	8	17	8.32	2.5	0.7	1.0	4.2	2.2	0.2	0.9	5.4	−27.8	−5.3
3140	7.97	16.2	1.06	5.1	0.1	1.5	4.8	3.9	0.2	1.7	5.9	−21.6	−3.4
8238	7.69	16.7	6.47	50.7	0.6	12.1	8.8	23.9	2.1	15.1	27.7	−28.4	−5.3

4.2. Major ions

Fig. 5 shows that strong acid anions (Cl^- and SO_4^{2-}) exceed weak acid anions (HCO_3^- and CO_3^{2-}). On the other hand, calcium and magnesium concentrations exceed sodium and potassium contents. This may indicate that groundwater can be classified into two water types that correspond to $\text{Ca-SO}_4\text{-Cl}$ and Na-Cl .

Bivariate plots provide insight into the contribution of particular ions to the groundwater mineralization and identify the major mineralization processes (Ben Moussa et al., 2012). Chlorides, sulfates, and nitrates display positive correlations with respect to the sum of anions. Sodium, calcium and magnesium exhibit strong relationships versus the sum of cations, indicating that these ions contribute largely to the groundwater salinization (Fig. 6).

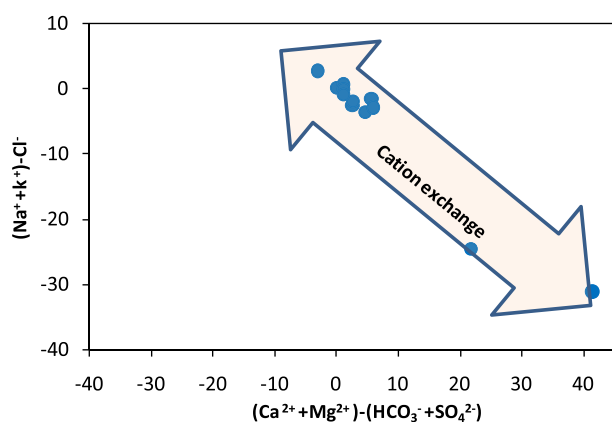
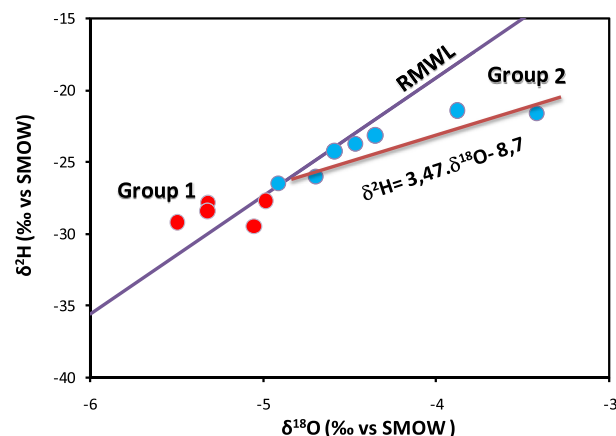
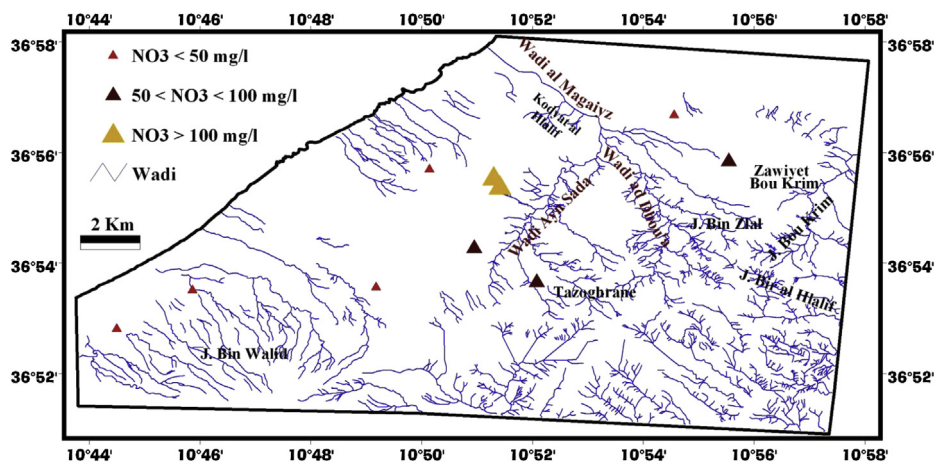
Fig. 9. Plot of $(\text{Na} + \text{K} - \text{Cl})$ versus $[(\text{Ca} + \text{Mg}) - (\text{SO}_4 + \text{HCO}_3)]$.Fig. 11. $\delta^{18}\text{O}/\delta^2\text{H}$ diagram.

Fig. 10. Spatial distribution of nitrate contents.

In the Na/Cl diagram, groundwater samples are plotted along a linear trend (Fig. 7a), reflecting a strong relationship between these elements, originating from the dissolution of halite. The effect of this dissolution is highlighted through the proportional evolution between the negative saturation indexes (Table 2) and the sum of ions ($\text{Na} + \text{Cl}$) (Fig. 7b). Calcium and sulfate contents show large variation with pronounced evolution along the assumed groundwater flow direction. Groundwater samples plotted in the plot of Ca versus SO_4 define a trend from calcium excess ($\text{Ca} > \text{SO}_4$) towards the 1:1 line, indicating the same origin of both ions in relation with the dissolution of gypsum and/or anhydrite minerals (Fig. 8a, b) (Dassi, 2004).

Table 2
Saturation index (SI) of the Tazoghrane shallow groundwater

Well	Saturation index		
	Halite	Gypsum	Anhydrite
7531	−5.48	−0.72	−0.95
249B	−6.31	−2.67	−2.92
249A	−6.16	−1.36	−1.61
217A	−6.82	−2.26	−2.51
217B	−4.46	−0.37	−0.62
221A	−5.07	−1	−1.25
221B	−5.76	−1.37	−1.61
69	−5.05	−1.51	−1.74
36	−5.58	−0.98	−1.23
8235	−6.93	−1.79	−2.03
3140	−6.37	−1.61	−1.85
8238	−4.69	−0.55	−0.79

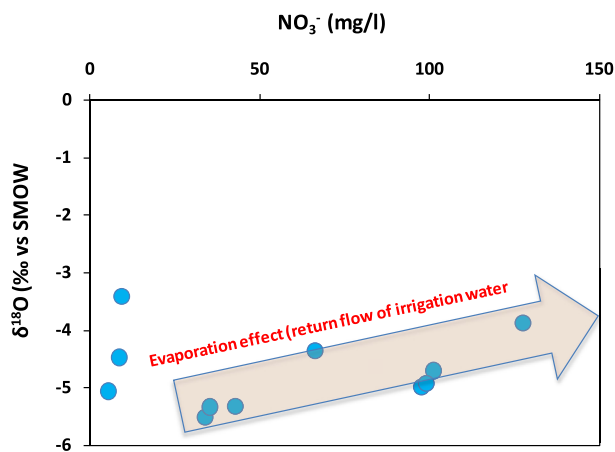


Fig. 12. Plots of $\delta^{18}\text{O}$ versus NO_3^- .

Detailed examination of Na/Cl and Ca/ SO_4 diagrams shows that the relative deficit of Na^+ with respect to Cl^- corresponds to an excess of Ca^{2+} with respect to SO_4^{2-} . This may indicate cation exchange as a major mineralization process of the Tazoghrane shallow groundwaters. The ion exchange is highlighted through the inverse proportional evolution between $(\text{Ca} + \text{Mg})-(\text{HCO}_3 + \text{SO}_4)$ and $(\text{Na} + \text{K}-\text{Cl})$ (Fig. 9) (Schoeller, 1965; Garcia et al., 2001).

4.3. Nitrate contents

Nitrate concentrations (Fig. 10) in the samples vary from 5.43 to 466 mg/l, and in about 60% of groundwater samples are greater than 50 mg/l (maximum European admissible nitrate concentration in drinking water). As the study region is one of the most important agricultural areas of the Cap Bon peninsula, intensive use of nitrogen fertilizers has profitably increased the agricultural production, with a negative impact on water quality. High nitrate contents appear to be related to areas of irrigation and application of fertilizers to shallow rooted vegetable crops on sandy soils. The proportional evolution between NO_3^-/Ca , K/NO_3 and Mg/SO_4 provide insight into the excessive use of $\text{Ca}(\text{NO}_3)_2$, KNO_3 and MgSO_4 fertilizers, respectively (Gi-Tak et al., 2004; Stigter et al., 2006).

4.4. Isotopes

Stable isotopic content of the Tazoghrane shallow groundwater ranges from -5.49 to -3.42‰ for $\delta^{18}\text{O}$ and from -29.49 to -21.42‰ for $\delta^2\text{H}$. Groundwater samples were plotted (Fig. 11) in the conventional diagram of $\delta^{18}\text{O}/\delta^2\text{H}$ with respect to the Regional Meteoric Water Line of Tunis Carthage (RMWL), given by $\delta^2\text{H} = 8 \delta^{18}\text{O} + 12.4$ (IAEA/WMO, 1999; Maliki et al., 2000). All groundwater samples are scattered around the RMWL indicating that the recharge of the Tazoghrane shallow aquifer originates from infiltration of recent precipitation from Mediterranean vapour masses.

Two groups of groundwater samples were identified based on their isotopic composition. The first group includes samples with relatively narrow ranges of $\delta^{18}\text{O}$ and $\delta^2\text{H}$ values, varying from -5.49 to -4.9‰ and from -29.49 to -23.5‰ , respectively. The relatively depleted isotopic values of the group 1 samples demonstrate the modern origin of these groundwaters, which are not affected by evaporated open water or soil water (Gat and Issar, 1974; Edmunds et al., 2003). The second group, which displays a relatively enriched $\delta^{18}\text{O}$ and $\delta^2\text{H}$ content, is placed below the RMWL and draws a regression line with the equation $\delta^2\text{H} = 3.47 \delta^{18}\text{O} - 8.7$. This line is characterized by relatively low values of the slope and the intercept, highlighting the evaporation effect of irrigation water return flow. The long-term practice of irrigation causes the infiltration of water that largely undergoes excessive

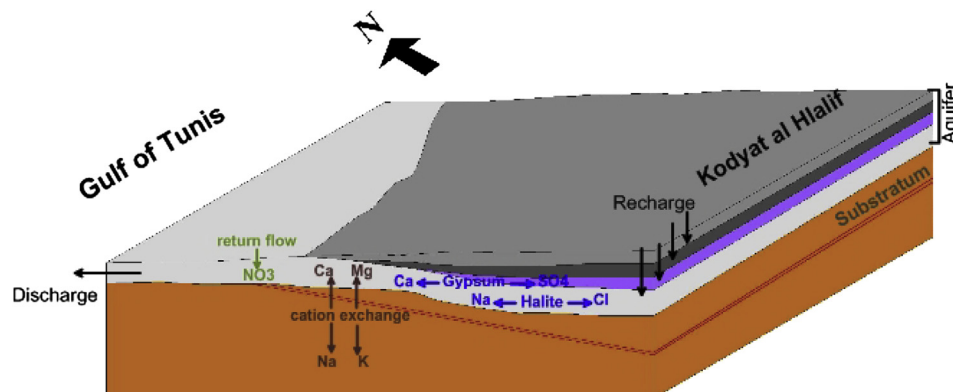


Fig. 13. Summary model of groundwater geochemical evolution in the Tazoghrane shallow aquifer.

evaporation in the soil and in the irrigation channels. Groundwater samples of the second group show a correlation between NO_3 and d^{18}O , reflecting the significant infiltration of evaporated irrigation water which is contaminated by nitrate fertilizer (Fig. 12).

5. Conclusions

Hydrochemical tracers in conjunction with environmental isotope methods were used to explore the origin and the mineralization processes of groundwater in the Tazoghrane aquifer. Groundwaters from the Quaternary shallow aquifer are dominated by two main water facies, $\text{Ca}-\text{SO}_4-\text{Cl}$ and $\text{Na}-\text{Cl}$, derived mainly from the dissolution of evaporates minerals (halite, gypsum and/or anhydrite) and cation-exchange processes (Fig. 13). Some groundwater samples, particularly from the agricultural districts, display high nitrate concentrations indicating the effect of irrigation return flow. Hydrogen and oxygen-18 stable isotopes signatures have identified waters not affected by significant evaporation, which suggests rapid infiltration before evaporation of meteoric waters. The stable isotope enrichment of groundwater samples collected from agricultural areas reflects the dominance of recharge by return flow of irrigation waters.

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