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Research paper

Geochemical characteristics of arid shallow aquifers in Chott Djerid, south-western Tunisia

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Abstract

A geochemical study using hydrochemical techniques and multivariate statistical analysis were undertaken to characterize shallow waters in southwestern Tunisia.

Hydrogeochemical investigations demonstrated that groundwater can be classified into different water facies either for the oasis or the Saharan shallow aquifers. The Kebili oasis shallow aquifers showed a Ca–SO₄ water type. The Douz and Djerid oasis shallow aquifers indicated a Na–Ca–Cl water type, whereas the Saharan shallow aquifers showed a Ca–HCO₃–NO₃ water type representative of the shallow waters in the piedmont of Dahar chain and a Na–Ca–SO₄–Cl water type representative of Saharan shallow waters with a TDS >2.2 g/l.

Compared to 2.2 g/l TDS limit, Q-mode hierarchical cluster analysis grouped 52 groundwater samples in two main groups: (1) the relatively less saline water (Group 1) and (2) the highly mineralized water (Group 2). The application of factor analysis to the datasets resulted in two factors, explaining 61.89% and 15.65% of the total variance. Those factors indicated that groundwater quality depended mainly on the dissolution of some evaporite minerals in the oasis shallow aquifers and the Saharan shallow aquifers with TDS >2.2 g/l. In addition, nitrate contamination (natural or anthropogenic) appeared to be a secondary process controlling the mineralization of the shallow aquifers located in the piedmont of Dahar chain. This pollution is local and related to the infiltration of livestock wastes and/or nitrification under reduced aquifer conditions. These waters were also characterized by the dissolution of carbonates and the cation exchange. The suitability of waters indicates that waters situated in the piedmont of Dahar could be used for drinking after precautions on nitrate contents. These waters associated with waters of the south west of Douz region could be used for the irrigation of date palms.

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1. Introduction

Water scarcity is a common feature of our modern world and this threat is predicted to be worse in the future. Population growth and economic development cause significant increases in agricultural (De Fraiture and Wichelns, 2009) and industrial demand for water. Agriculture accounts for more than two thirds of the global water use. This situation may induce severe water

crisis (Varghese et al., 2012) and all waters even those of bad quality have to be valued and stored. Therefore, the past few decades have witnessed a rising in the study of surface waters (i.e., the shallow aquifers in arid regions).

The southwestern part of Tunisia is characterized by the presence of very important non-renewable groundwater resources of the Continental Intercalaire (CI) and the Complex Terminal (CT) (OSS, 2003) and by shallow aquifers, though considered of secondary importance (Zammouri et al., 2007; Kamel, 2011; Kraiem et al., 2012). Although, groundwater is often the only reliable source of fresh water in arid and semi

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arid regions, shallow waters were also extensively studied and characterized for domestic or agricultural use (Guendouz et al., 2006; Gattacceca et al., 2009; Garcia-Garizabal and Causapé, 2010; Heagle et al., 2012). In those areas, water bodies of oases are mainly used by farmers for irrigation during summer drought because of the cost of the water distribution and to complement the official water allotment. Saharan waters were used as a drink for both human and animals. Some water points located in the wadi el Hallouf, in the piedmont of Dahar were used as drinking sources for the populated areas of Kebili and Douz regions. These waters are carried in tanks towards the designated regions. Consequently, a chemical characterization seems to be necessary to determine the suitability of these waters for irrigation and drinking purposes.

This study focused on shallow aquifers situated along the shoreline of Chott Djerid, a large hyper saline depression in southwestern Tunisia submitted to arid and hyper arid climate, to (1) characterize those shallow resources and (2) manage them in terms of water conservation and sustainable development. These resources are defined by variable quantity and quality through heterogenous salinity distribution.

2. Site description

2.1. Climate and location of the study area

The study area belongs to the northern edge of the Sahara desert (southwestern of Tunisia). It is bordered by the northern range of the Chott to the north, the Tebaga mountainous chain to the northeast and the Tozeur uplift to the west; it opens on the Grand Erg Oriental southwards (Fig. 1). The area is marked by the presence of a vast nearby salt depression (i.e., Chott Djerid) and by an arid to hyper arid climate with less

than 100 mm per year of rainfall. The average of daily temperatures varied between 10 °C in winter and 32 °C in summer, august being the hottest month. The yearly open water evaporation is about 2500 mm in the Saharan zone (Zammouri et al., 2007) and 1700 mm in the oasis.

One of the characteristics of the region is the concentration of the populated area near the oases in the borders of Chott Djerid. The remaining of the region is completely bare soil with local pastoral activities.

2.2. Geology and hydrogeology

Previous studies indicated that the survey area is a sedimentary basin in which aquifer levels are stratified with lateral and vertical communications due to lenticular layers (OSS, 2003). These levels are characterized by high heterogeneities in geological and hydrogeological features. Shallow aquifers are contained in the upper level of Plio-Quaternary formations part of the huge set of sand dunes known as the Grand Erg Oriental (OSS, 2003). They are classified either oasis or Saharan according to their geographical location. Saharan shallow aquifers supplying drinking water or pasture needs in particular in wadis underflows are distinguished from oasis shallow aquifers used for backup supplies in times of extreme water shortages. These oasis shallow aquifers have been observed during field trips to be mainly lodged near surface formations with clayey sand lithology, while Saharan shallow aquifers are hosted by various formations according to their spatial distribution. Situated on the shorelines of Chott Djerid, the oasis shallow aquifers were stored in the superficial fillings essentially with clayey sand and gypsum formations. For the Saharan shallow aquifers, formations were essentially with silt and alluvium of wadis (OSS, 2003).

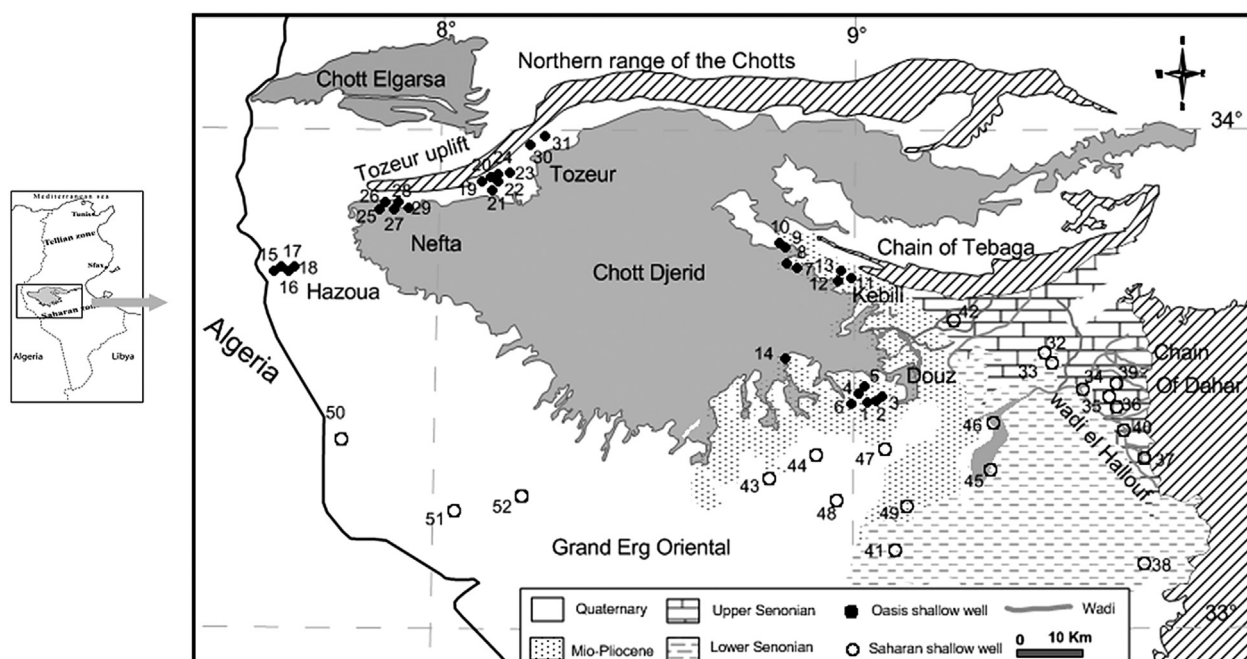


Fig. 1. Location and geologic setting of the studied area.

Shallow aquifers could be characterized according to their recharge modes, piezometry and water losses. Shallow waters had been stored during rainy periods of the Plio-Quaternary recognized as the main groundwater recharge period in southern Tunisia (OSS, 2003; Edmunds et al., 1997; Zouari et al., 2003). Nowadays, Saharan shallow aquifers are recharged during the rare rainfall events occurring under hyper arid climate as for oasis ones, recharge is essentially ensured by the infiltration of irrigation waters (OSS, 2003).

The piezometric map of the shallow aquifers situated in the eastern part of Chott Djerid is shown in Fig. 2. This figure represents measurements of groundwater levels carried out in April 2008 where the main subsurface flow direction is broadly from south and east towards Chott Djerid. The high piezometric gradient observed in the Dahar chain decreased regularly towards Chott Djerid, indicating the importance of this chain in the recharge of shallow aquifers (those located near the Dahar piedmont). The Tebaga chain also constitutes a secondary zone of recharge. The Chott Djerid and the south west of Douz constitute the natural discharge areas of these shallow aquifers.

3. Materials and methods

3.1. Water sampling and chemical analysis

A total of 52 water samples were collected during two sampling campaigns carried out in April 2008 and in April 2009 at boreholes in various parts of the study area (Fig. 1). In April 2008, 14 samples were taken from the oasis shallow aquifers of Kebili and Douz areas, and 31 samples from the Saharan shallow aquifers. In 2009, 17 samples were taken from the western part of Chott Djerid (i.e., the oasis shallow

aquifers). In total, 31 samples from the oasis aquifers along the shorelines of Chott Djerid and 21 samples from the Saharan shallow aquifers were used for the present study. The depth of the water samples is represented near the surface of the water after purging of the well.

Groundwater samples were filtered through 0.45 μm acetate cellulose filter. Temperature (T_{re} ($^{\circ}\text{C}$)), electrical conductivity (EC) and pH were measured on site using a HI 9828 Multi-parameter. To determine major and minor element concentrations, water samples were collected and stored in polyethylene bottle that were pre-treated with diluted nitric acid and then rinsed twice with distilled water and groundwater. Nitric acid (HNO_3) was added to aliquots devoted to cationic analyses. Volumetric titrations were performed to determine the bicarbonate alkalinity.

Chemical analyses of major elements (Na^+ , Ca^{2+} , Mg^{2+} , K^+ , Cl^- , SO_4^{2-} , HCO_3^- and CO_3^{2-}) and nitrates (NO_3^-) were carried out in the Laboratory of Radio-Analyses and Environment (LRAE) of the National School of Engineers of Sfax (Tunisia) by Liquid-Ion Chromatography (HPLC) on a water chromatograph equipped with columns IC-PakTM CM/D for cations, using EDTA and nitric acid as eluent, and on a Metrohm chromatograph equipped with columns CI SUPER-SEP for anions using phthalic acid and acetonitrilic as eluent. The test precision of the instrument is about $\pm 2\%$. The overall detection limit for ions was 0.04 mg/l. The total alkalinity (as HCO_3^-) was determined by titration with 0.01 or 0.1 HCl against methyl orange and bromocresol green indicators. Salinity of water represents the total dissolved salts (TDS) defined as the concentration of dissolved salts in g/l.

The quality of the chemical analyses was also checked by running the test of charge balance error according to Freeze and Cherry (1979): charge Balance error (%) = $100 \times ((\Sigma$

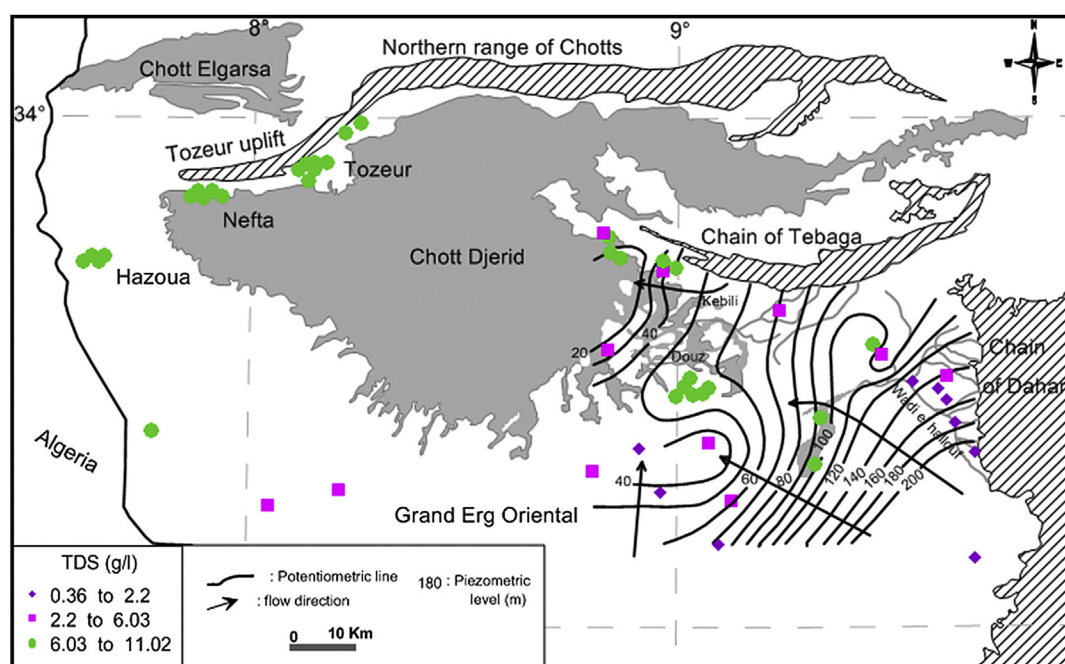


Fig. 2. Piezometric and salinity map of shallow aquifers in the studied area.

$z \cdot m_c - \sum z \cdot m_a / (\sum z \cdot m_c + \sum z \cdot m_a)$). Where z is the absolute value of the ionic valence, m_c is the molality of cationic species, and m_a is the molality of the anionic species. For all samples, the analytical error inferred from the balance between cations and anions did not exceed 5%.

Major elements were plotted on the piper diagram in order to identify water chemical facies. Bivariate diagrams of $\text{Ca}^{2+}/(\text{SO}_4^{2-})$ and $\text{NO}_3^-/(\text{Ca}^{2+})$ were plotted to investigate the causes and mechanisms of the geochemical processes controlling water mineralization and quality. Some molar ratios of $(\text{Na}^+/\text{Cl}^-)$, $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $\text{SO}_4^{2-}/\text{Cl}^-$ vs. Cl^- were also established.

3.2. Statistical analysis

While hydrochemistry diagrams reflect relationships between two variables only, the statistical analysis gives relationships between a large number of variables. So, water chemical data has also been approached using a bivariate analysis (correlation matrix) and a multivariate analysis (Hierarchical Clustering Analysis (HCA) and Factor Analysis (FA)).

The Hierarchical Clustering Analysis associated with the Factor Analysis led to the classification of the water samples into separate groups and the evaluation of variations and similarities among them on the basis of their hydrochemical characteristics.

3.2.1. Hierarchical Clustering Analysis (HCA)

Hierarchical Clustering Analysis technique is commonly used to classify samples into similar groups based on their chemical composition (Aruga et al., 1995; Suk and Lee, 1999). 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 among them, while Q-mode reveals the interactions among the studied samples (Davis, 2002). In this study, Q mode hierarchical clustering analysis is based on the Ward's linkage method (Ward, 1963) that uses squared Euclidean distances as a measure of similarity between samples.

3.2.2. Factor Analysis (FA)

Factor Analysis is a multivariate statistical commonly used to find out possible relationships between several variables and to synthesize information in a series of factors or components (Davis, 2002). This method enables a generic interpretation of the environment through the creation of new groups of variables by linear combinations of the original data. In general, the first factor accounts for most of the total variance in the dataset and the following factors cumulate the remaining small portions of this variance. Interpretation is based on factor loadings and factor scores. The factor loadings indicate how the factors characterize the variables while factor scores indicate how each sample may be linked to the intensity of the chemical processes described by these factors (Dalton and Upchurch, 1978). A high factor loading, trending to the unity (either positive or negative), shows a strong relationship between the variables and this factor. On the other hand,

extreme positive values of factor scores ($>+1$) reflect the most affected areas by the chemical process represented by this factor while negative values (<-1) reflect the non-impacted areas. Between these two extreme values, the impact of the chemical process on the variable is considered to be of moderate degree. The spatial distribution of the factors representing the hydrochemical process can be determined by a contour map of the factor scores.

4. Results and discussion

4.1. Hydrochemistry

Having similar climatic conditions, our sampling in the study area was carried out over two years during the same season (2008 and 2009) on the shorelines of Chott Djerid. The use of water is the same, essentially for agricultural activities of date palms.

4.1.1. Physical parameters

Geochemical characteristics of the water samples are presented in Table 1. The physical and chemical parameters of shallow waters indicated large spatial variations. The pH values ranged from 6.2 to 8.1. Relatively high values characterize Saharan shallow aquifers, especially those of the Dahar piedmont. It can be explained by the presence of basic elements such as nitrates which are abundant in this area. Furthermore, lithological formations contain limestone, an environment where several redox reactions may occur inducing dissolution of carbonates. Temperature ($^{\circ}\text{C}$) has an average of 20°C and does not present remarkable variations.

Electrical conductivities (EC) and total dissolved salt (TDS) values have heterogeneous distributions as illustrated by Fig. 2. Low values ($\text{TDS} < 2.2 \text{ g/l}$) were recorded for water sampled along the Dahar piedmont and for some samples from the southern part of the Douz region (sample no. 41, 43, 44 and 48). They correspond to the recharge zone as illustrated by the piezometric map (Fig. 2). The second group has a salinity varying between 2.2 and 6 g/l. It characterizes some samples taken from the oasis and Saharan shallow aquifers with a tolerable salinity up to 6 g/l, which can be locally used for irrigation of date palms for the sustainable development of water and soil. The third group has salinity values greater than this limit. These waters were considered high-mineralized and constitute the majority of the oases shallow aquifers. They are concentrated near Chott Djerid which constitutes the discharge area of the piezometric water flow. The use of these waters for irrigation could represent a degradation risk for the soil agriculture potential. The heterogeneous distribution of salinity may be related to several factors such as evaporites (halite, gypsum and/or anhydrite and sylvite) dissolution, accumulation and infiltration of salted water coming from irrigation excess flow and the evaporation effect. Salinity could also be related to the intrusion of drainage water accumulated in low depressions or basins on the shorelines of oases (Kraiem et al., 2012).

Table 1
Geochemical characteristics of the analyzed samples in the study area.

Sample n°	Depth (m)	EC (S/cm)	Tre (°C)	pH	Cl	SO ₄	CO ₃	HCO ₃ (meq/l)	NO ₃	Na	Mg	K	Ca	TDS (g/l)	SAR	SI Anhy.	SI Arag.	SI Cal.	SI Dol.	SI Gyp.	SI Hal.
1	8	13.3	19.7	7.2	117.7	63.0	0.0	5.8	0.0	99.0	38.4	1.88	53.9	10.7	14.5	−0.1	0.6	0.7	1.5	0.1	−3.8
2	8.7	12.0	18.2	7.7	98.5	52.5	0.0	2.6	0.0	91.7	22.9	1.90	42.9	10.0	15.9	−0.2	0.7	0.8	1.5	0.0	−3.9
3	15.7	8.8	22.2	7.2	57.4	37.0	0.0	3.4	1.4	28.9	30.5	0.00	42.7	6.6	4.8	−0.3	0.4	0.5	1.0	−0.1	−4.6
4	7.7	11.2	21.2	7.2	75.6	47.0	0.0	6.6	0.0	58.7	30.1	1.46	43.1	9.1	9.7	−0.2	0.6	0.7	1.4	0.0	−4.2
5	7.5	11.3	19.9	7.6	77.6	72.4	0.0	2.8	0.0	68.3	40.2	5.52	44.5	9.3	10.5	−0.1	1.0	1.2	2.5	0.1	−4.1
6	6.8	9.4	19.6	7.7	54.0	57.7	0.0	6.4	0.0	44.1	38.8	0.00	37.9	8.1	7.1	−0.2	1.0	1.2	2.5	0.0	−4.5
7	3.9	10.3	19.7	7.3	71.4	68.8	1.0	5.9	0.0	56.5	42.8	1.82	45.0	8.8	8.5	−0.1	0.6	0.8	1.6	0.1	−4.2
8	6.1	8.9	19.9	7.8	50.6	54.9	1.4	3.3	0.0	44.0	29.6	1.41	29.9	7.1	8.0	−0.3	0.7	0.9	1.9	−0.1	−4.5
9	7.4	7.2	23.5	7.0	40.5	51.2	0.8	4.7	0.0	34.3	20.0	1.89	34.6	6.0	6.6	−0.2	0.2	0.4	0.6	0.0	−4.7
10	5.1	5.8	22.2	7.4	29.8	44.1	0.4	3.9	0.0	22.9	12.0	1.68	36.2	5.0	4.7	−0.2	0.6	0.7	1.1	0.0	−5.0
11	4.6	7.6	20.8	7.6	47.4	51.7	0.0	5.0	0.3	40.0	23.5	1.09	37.2	6.2	7.2	−0.2	0.8	1.0	1.9	0.0	−4.6
12	7.5	7.2	21.5	6.8	39.6	46.8	0.0	6.2	0.0	35.4	19.5	0.09	40.0	6.0	6.5	−0.2	0.2	0.3	0.5	0.0	−4.7
13	5	9.1	20.5	7.7	57.5	59.1	0.2	4.8	0.1	50.0	29.9	1.26	37.9	7.5	8.6	−0.2	0.9	1.1	2.1	0.0	−4.4
14	6.5	5.7	21.1	7.9	30.1	47.3	0.8	4.2	0.1	21.7	14.0	1.35	38.7	5.0	4.2	−0.2	1.1	1.2	2.1	0.1	−5.0
15	6	7.8	17.3	6.3	45.8	53.3	0.0	5.3	0.1	45.0	23.0	1.53	38.1	7.0	8.1	−0.2	−0.4	−0.3	−0.6	0.0	−4.5
16	6	8.4	17.4	6.3	47.6	50.6	0.0	6.1	0.1	45.3	22.0	0.78	36.1	7.1	8.4	−0.2	−0.4	−0.2	−0.5	0.0	−4.5
17	5.5	7.8	16.0	6.4	39.4	55.7	0.0	6.1	0.1	38.6	20.3	1.20	34.3	6.8	7.4	−0.2	−0.3	−0.2	−0.5	0.0	−4.6
18		9.0	21.0	6.4	57.2	54.8	0.0	8.6	0.1	56.0	27.4	1.28	39.8	7.8	9.6	−0.2	−0.2	0.0	−0.1	0.0	−4.3
19	7	7.4	25.8	6.2	37.9	57.0	0.0	6.7	0.1	35.5	30.5	1.92	35.5	6.7	6.2	−0.2	−0.5	−0.3	−0.6	0.0	−4.7
20	50	7.8	25.4	6.4	45.4	50.8	0.0	13.5	0.0	35.3	27.0	1.69	35.1	6.8	6.3	−0.3	0.1	0.2	0.4	0.0	−4.6
21	8	10.8	23.6	6.4	65.3	67.7	0.0	6.0	0.1	61.1	40.6	2.01	34.0	9.3	10.0	−0.2	−0.4	−0.3	−0.3	0.0	−4.2
22	50	8.2	21.9	6.3	47.3	53.5	0.0	14.7	0.1	43.1	31.9	1.30	37.6	7.3	7.3	−0.2	0.0	0.1	0.3	0.0	−4.5
23	20	10.5	19.7	6.4	64.5	64.7	0.0	8.2	0.1	59.7	36.7	2.27	34.2	9.1	10.0	−0.2	−0.2	−0.1	0.0	0.0	−4.3
24	8	9.4	19.5	6.3	58.5	59.3	0.0	7.7	0.2	55.0	34.2	1.31	36.1	8.1	9.2	−0.2	−0.3	−0.2	−0.2	0.0	−4.3
25		10.3	23.1	6.4	74.4	51.0	0.0	5.0	0.0	68.1	23.6	2.50	31.9	8.2	12.9	−0.3	−0.5	−0.3	−0.7	−0.1	−4.1
26		8.2	26.3	6.3	42.6	42.1	0.0	5.0	0.3	40.8	21.1	1.38	28.8	6.1	8.1	−0.4	−0.5	−0.4	−0.8	−0.1	−4.6
27	8.3	7.82	20.8	6.3	41.6	55.5	0.0	6.0	0.0	40.3	23.3	1.48	37.5	6.3	7.3	−0.2	−0.4	−0.2	−0.6	0.0	−4.6
28	8	8.60	19.9	7.5	39.4	56.4	0.0	6.4	0.1	36.2	28.4	0.73	38.4	6.9	6.3	−0.2	0.8	0.9	1.9	0.0	−4.7
29	12	7.68	20.3	6.3	39.3	52.2	0.0	5.4	0.1	35.4	22.8	2.07	35.7	6.1	6.5	−0.2	−0.5	−0.3	−0.7	0.0	−4.7
30	50	9.1	24.0	6.3	60.6	45.8	0.0	6.8	0.1	51.5	25.7	1.40	37.5	7.6	9.1	−0.3	−0.3	−0.2	−0.4	−0.1	−4.3
31	7	12.4	25.7	6.3	90.0	71.0	0.0	6.0	0.1	81.4	37.9	2.32	41.8	11.0	12.9	−0.2	−0.4	−0.3	−0.4	0.1	−4.0
32	21.9	9.7	19.4	7.8	44.0	59.3	0.0	1.8	9.1	59.2	15.8	6.48	33.7	7.9	11.9	−0.2	0.5	0.6	1.0	0.0	−4.4
33	30.4	4.1	22.4	7.9	10.0	40.3	0.0	1.4	1.8	16.5	11.2	0.43	28.2	3.7	3.7	−0.3	0.5	0.6	1.0	−0.1	−5.6
34	11.3	1.3	21.0	8.1	2.7	7.6	0.0	1.8	0.5	4.5	3.0	0.17	6.1	0.9	2.1	−1.2	0.5	0.6	1.1	−1.0	−6.6
35	8.1	0.8	18.3	7.9	1.0	3.7	0.0	3.3	0.5	1.7	2.4	0.08	4.5	0.6	0.9	−1.6	0.5	0.6	1.1	−1.3	−7.5
36	5	0.5	20.8	8.2	0.7	1.9	0.6	1.7	0.7	1.0	1.4	0.09	2.9	0.4	0.7	−1.9	0.3	0.4	0.7	−1.7	−7.8
37	9.4	0.6	22.1	8.1	1.0	2.1	0.0	1.4	1.1	1.6	1.3	0.26	2.4	0.4	1.2	−2.0	0.1	0.2	0.3	−1.8	−7.5
38	8.4	2.5	20.7	7.7	8.1	12.8	0.0	2.0	6.9	9.6	7.1	0.11	10.5	1.9	3.2	−0.9	0.2	0.4	0.7	−0.7	−5.9
39	7.1	2.8	19.4	7.9	2.7	31.5	0.0	4.4	1.5	5.4	6.5	0.60	25.2	2.6	1.3	−0.3	1.0	1.2	1.8	−0.1	−6.6
40	44	0.7	17.4	7.5	0.9	3.4	0.0	2.5	0.0	2.0	1.8	0.00	3.5	0.5	1.2	−1.7	−0.1	0.0	−0.2	−1.4	−7.4
41	33.1	0.7	20.9	7.7	2.9	2.0	0.0	2.0	0.0	2.7	2.3	0.17	2.1	0.5	1.8	−2.1	−0.3	−0.1	0.0	−1.9	−6.8
42		5.0	20.1	7.5	17.6	39.4	0.0	1.2	1.7	14.6	9.7	1.83	33.4	4.1	3.1	−0.2	0.1	0.3	0.1	0.0	−5.4
43		2.9	18.2	7.7	16.9	15.8	0.0	2.1	0.5	12.1	5.6	0.00	20.9	2.3	3.3	−0.7	0.5	0.7	0.9	−0.4	−5.4
44		2.4	17.7	8.0	8.5	10.3	0.6	2.1	0.4	8.8	4.5	0.00	10.1	1.6	3.3	−1.0	0.6	0.7	1.2	−0.8	−5.9
45		7.8	20.9	7.7	34.0	52.4	0.0	1.9	0.0	34.0	20.5	4.22	32.8	6.2	6.6	−0.2	−0.2	−0.1	−0.3	0.0	−4.8
46		11.5	19.1	7.8	94.0	42.9	0.0	2.1	2.1	71.5	25.2	0.92	33.6	8.2	13.1	−0.4	0.6	0.7	1.4	−0.1	−4.0

(continued on next page)

Table 1 (continued)

Sample n°	Depth (m)	EC (S/cm)	Tre (°C)	pH	Cl	SO ₄	CO ₃	HCO ₃ (meq/l)	NO ₃	Na	Mg	K	Ca	TDS (g/l)	SAR	SI Anhy.	SI Arag.	SI Cal.	SI Dol.	SI Gyp.	SI Hal.
47	17.7	6.2	21.0	7.7	42.8	24.4	0.0	2.8	0.1	30.8	13.1	0.17	27.6	4.7	6.8	-0.5	0.6	0.8	1.4	-0.3	-4.7
48	10.6	2.5	21.0	7.6	10.0	8.8	0.0	1.7	1.0	9.2	4.8	0.59	7.6	1.4	3.7	-1.2	0.0	0.1	0.2	-0.9	-5.8
49	8.8	8.5	20.7	7.5	49.0	36.5	0.0	2.3	0.0	49.1	16.2	1.37	20.3	5.2	11.5	-0.5	0.2	0.3	0.7	-0.3	-4.4
50		9.0	19.6	7.9	70.8	45.1	0.0	0.4	0.8	49.7	18.4	0.00	51.4	7.2	8.4	-0.2	0.2	0.3	0.3	0.1	-4.3
51		5.8	23.8	7.7	30.2	32.4	0.0	1.5	1.3	28.4	9.0	0.00	34.9	4.6	6.0	-0.3	0.5	0.6	0.8	-0.1	-4.9
52		5.8	23.1	7.4	27.7	45.5	1.2	5.3	0.7	26.5	14.0	0.00	40.4	5.1	5.1	-0.2	0.7	0.9	1.4	0.1	-4.9

EC: electrical conductivity (S/cm); Tre: temperature in °C; TDS: total dissolved salts; SAR: sodium absorption ratio; SI: saturation indices of (Anhy.: anhydrite; Arag.: aragonite; Cal.: calcite; Dol.: dolomite; Gyp.: gypsum and Hal.: halite).

4.1.2. Hydrochemical facies

The major ions plotted on the trilinear Piper diagram (Fig. 3(a) and (b)), allow to differentiate different water types. Nitrate contents were taken into account because of their relative abundance in these waters. The oasis and Saharan shallow aquifers were plotted separately on the piper diagram shown in Fig. 3(a) and (b), respectively. The Kebili oasis shallow aquifers showed a Ca–SO₄ water type. However, Douz and Djerid oasis shallow aquifers showed a Ca–Na–Cl water type (Fig. 3(a)). For the Saharan shallow aquifers, we distinguished two water types (Fig. 3(b)): (1) a Ca–NO₃–HCO₃ water type representative of the Saharan shallow waters located in the piedmont of the Dahar chain and (2) a Ca–Na–SO₄–Cl representing the remaining Saharan shallow waters. The heterogeneity in the water type distributions could be related to the variety of water mineralization processes occurring in these regions.

4.1.3. Concentration and sources of major ions

In order to specify the probable origin of each major element contributing to the water mineralization, relationships between some major elements were established. Sulfate concentrations were plotted vs. calcium, they showed relatively high values, especially in the oasis shallow aquifers and some Saharan shallow waters (Fig. 4). These concentrations may be explained by the dissolution of superficial saline gypsum crusts during recharge and/or irrigation return flow. Moreover, the loss of Ca²⁺ with respect to SO₄²⁻ may be the result of calcite and aragonite precipitation controlled by gypsum dissolution which tends to maintain saturation or oversaturation with respect to calcite and aragonite bearing minerals.

In fact, water saturation states for minerals as anhydrite (SI anh.), gypsum (SI gyp.), halite (SI hal.), calcite (SI cal.) and dolomite (SI dol.) were computed (Table 1). If the SI is <0, dissolution is considered as the dominant process for the related mineral and when the SI is >0, precipitation of the mineral is likely to be occurring in the system (Freeze and Cherry, 1979).

Fig. 5 demonstrated that Djerid oasis shallow aquifers, situated along the western part of the Chott, are undersaturated with respect to carbonate minerals (calcite, aragonite and dolomite). Indeed, dissolution of halite, gypsum and anhydrite is also confirmed through the parabolic proportional relationships in the plots of (Na⁺ + Cl⁻) and (Ca²⁺ + SO₄²⁻) against saturation indices of waters with respect to referred minerals (Fig. 5) (Sacks and Tihansky, 1996).

The Na⁺/Cl⁻ molar ratio (Fig. 6) is relatively constant for the major samples and around 1 indicating that dissolution constitutes the main process occurring in waters sampled from the oasis shallow aquifers and from Saharan shallow aquifers with TDS more than 2.2 g/l. However, some samples indicated higher Na⁺/Cl⁻ molar ratio, reaching 2 in some cases. These points represent samples taken from the Saharan shallow aquifers situated in the wadis beds. In this area, Mio-Plio-Quaternary formations lodging shallow aquifers contain low but significant clay sediments. The excess of Na⁺ vs. Cl⁻ may be explained by a cation exchange. These processes could also

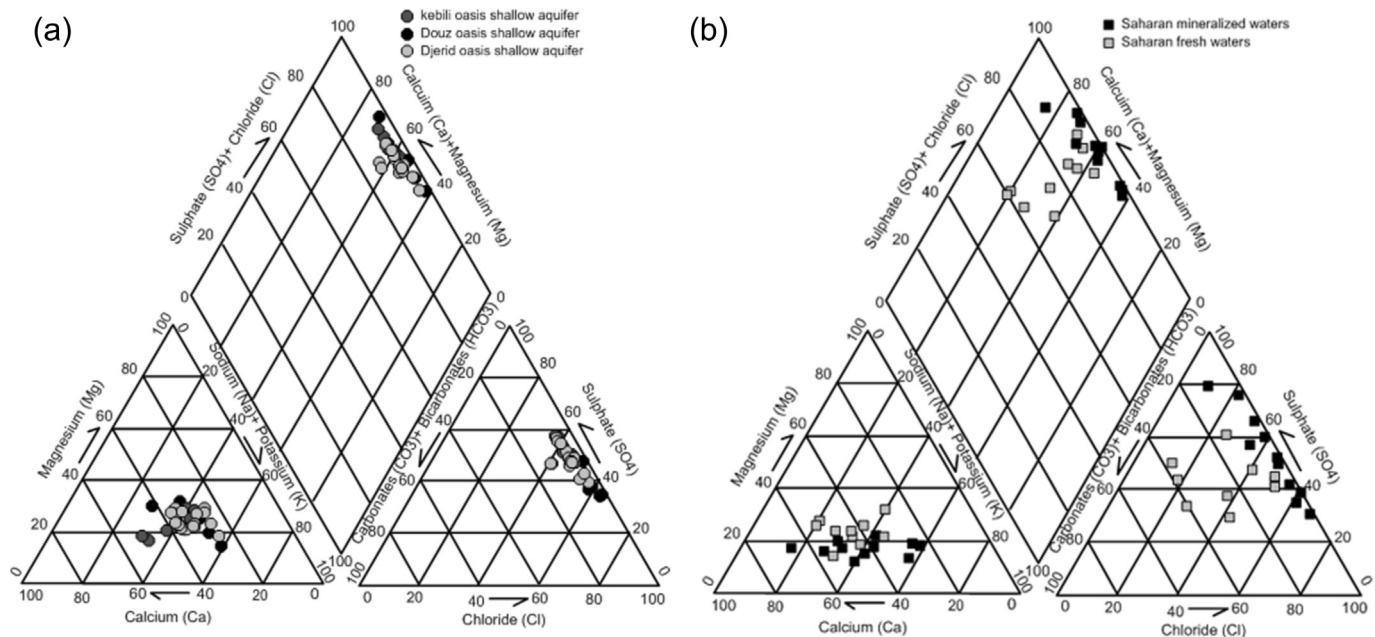


Fig. 3. Piper diagrams of the oasis shallow samples (a), and the Saharan shallow samples (b).

be demonstrated by the plot of Na^+/Cl^- ratio vs. $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$, (Fig. 7).

High $\text{SO}_4^{2-}/\text{Cl}^-$ molar ratios were also observed; they ranged between 2 and 12 in most cases, confirming that ions are monitored by their respective solubilities (Fig. 6). Some $\text{Mg}^{2+}/\text{Ca}^{2+}$ molar ratios are under 1, probably because of the excess in calcium contents related to cationic exchanges (Fig. 6).

4.2. Statistical analysis

The statistical analyses were undertaken for 10 hydrochemical variables including TDS, Cl^- , Na^+ , Mg^{2+} , HCO_3^- , SO_4^{2-} , K^+ , Ca^{2+} , NO_3^- and pH considered as the most

important analyzed parameters representing the mineralization and the contamination in this region. All the samples were analyzed using a correlation matrix, a cluster analysis and a factor analysis.

4.2.1. Correlation matrix

The correlation matrix is used to study and distinguish the relevant hydrochemical relationships between the different parameters. Correlation coefficients between variables are presented in Table 2. Contents of chloride, sulfate, sodium, magnesium and calcium are positively correlated to the total dissolved salts with correlation coefficients of 0.93; 0.93; 0.94; 0.92 and 0.88, respectively, indicating that these elements are contributing to water mineralization and proving the correlations between the major elements and TDS.

The good correlation between chloride and sodium ($R^2 = 0.97$) confirms their same origin, that is, the dissolution of the halite resulting from the action of surface waters on salts. For all the waters, magnesium concentrations are positively correlated with calcium concentration ($R^2 = 0.77$). The presence of magnesium in these waters might be due to the alteration and dissolution of dolomites. Sulfate concentrations are tightly correlated to the presence of calcium, sodium and magnesium which is explained by the dissolution of evaporite minerals and the cation exchange in the clay minerals. Nitrates haven't correlation neither with the major elements nor with the TDS, indicating their anthropogenic origin.

4.2.2. Hierarchical Cluster Analysis (HCA)

As there is no test to determine the optimum number of groups in the dataset (Güler et al., 2002), the visual inspection is the only criteria to select the groups in the dendrogram (Fig. 8). The defined phenon line (Sneath and Sokal, 1973) was chosen at

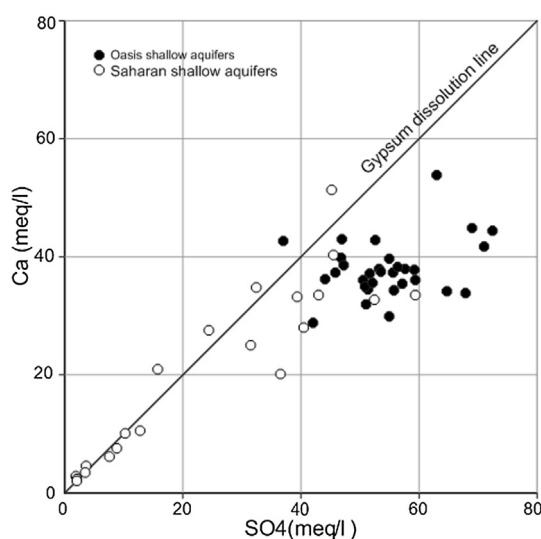


Fig. 4. Ca^{2+} vs. SO_4^{2-} relationship.

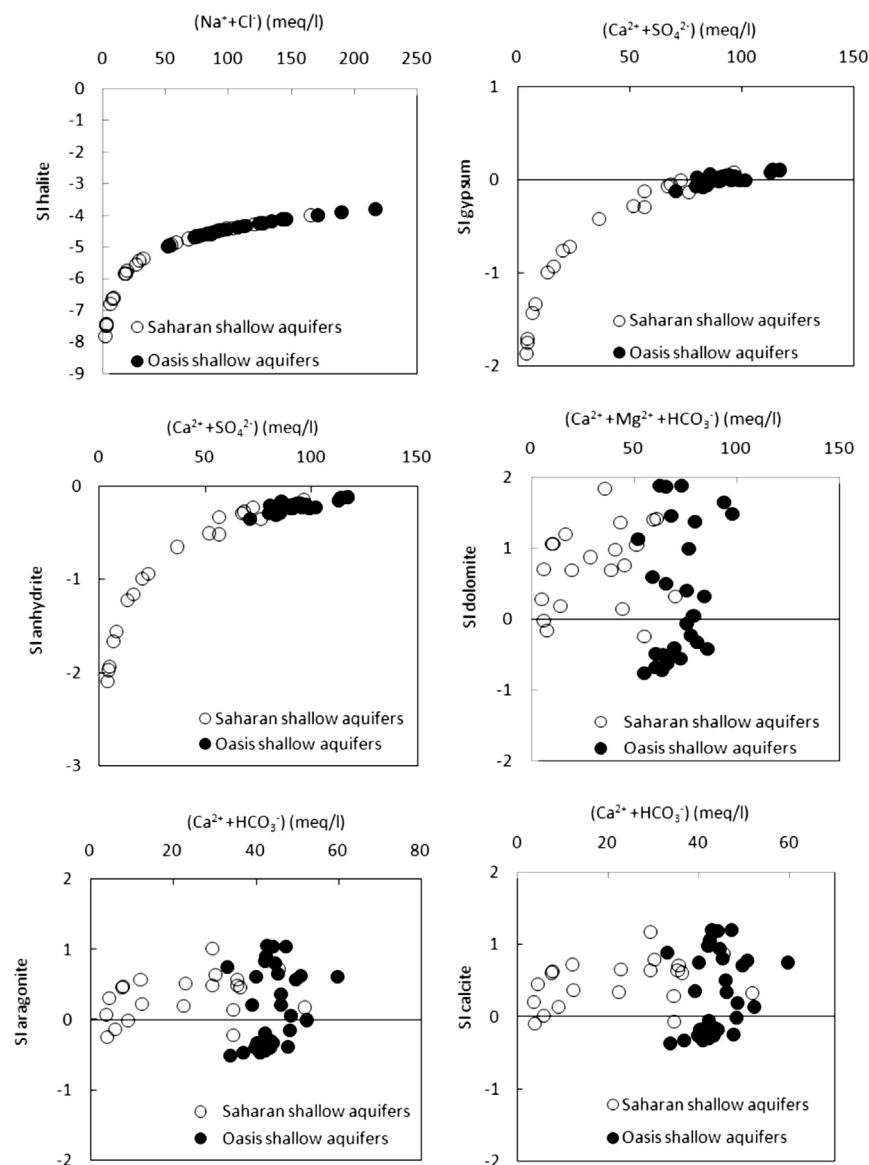


Fig. 5. Plots of Saturated Indices (SI) with respect to some carbonate and evaporite minerals.

a linkage distance of 900. At this distance, we can distinguish the groups in terms of their hydrochemical variables.

In total, two groups were distinguished: (1) Group 1 is made up of 10 wells represented by samples no. 43, 38, 48, 44, 41, 37, 36, 40, 35 and 34 which were sampled from the Saharan shallow aquifers with $TDS < 2.2$ g/l; (2) Group 2 includes the rest of the observations with $TDS > 2.2$ g/l and defines the oasis shallow aquifers of Douz, Kebili and Djerid regions and the remaining of the Saharan shallow aquifers. The results of the HCA show that the most discriminating parameter used in grouping the samples is TDS. This parameter has a mean of 1039 mg/l and 6974.5 mg/l for group 1 and group 2, respectively.

4.2.3. Factor Analysis (FA)

The Kaiser criterion (Kaiser, 1960) was applied to determine the total number of factors that could summarize the dataset. Under this criterion, only factors with eigenvalues

greater than or equal to 1 will be considered as possible sources of variance in the data, with the highest priority ascribed to the factor that has the highest eigenvector sum. The rationale for choosing 1 is that a factor must have a variance which is at least as large as that of a single standardized original variable to be acceptable.

Results from FA are more efficient when the number of factors is small. Similarities are high (close to 1) and the factors are easily interpretable with regard to sources or processes. A set of physical–chemical parameters correlated with a particular factor can be explained through a chemical process (anthropogenic or geogenic) which can lead to the observed variability in the dataset.

Eigenvalues of the first two factors (F1 and F2) and their cumulative percentage of variance are presented in Table 3. The eigenvalues of the 2 first factors exceeding 1 explain 77.54% of the total variance.

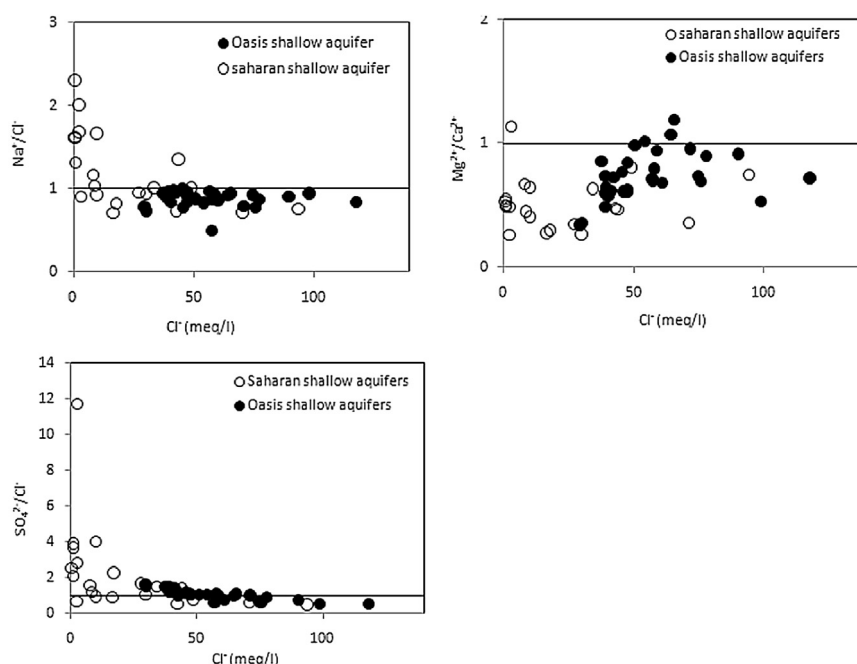


Fig. 6. (Na^+/Cl^- , $\text{Mg}^{2+}/\text{Ca}^{2+}$ and $\text{SO}_4^{2-}/\text{Cl}^-$) vs. Cl^- relationships.

Fig. 9 shows the relationship between F1 and F2 factor loadings. Factor 1 has the highest factor loadings of Na^+ , Ca^{2+} , Mg^{2+} , Cl^- , SO_4^{2-} , K^+ and TDS. It accounts for 61.89% of the total variance. This axis reflects the role of natural factors such as dissolution of evaporite minerals of the observed mineralization. Factor 2 is characterized by high factor loadings of HCO_3^- (positive), pH (negative) and NO_3^- (negative) and accounts for 15.65% of the total variance. The opposite evolution of HCO_3^- and (pH, NO_3^-) (Fig. 9) could be explained by the carbonate weathering and could reflect the influence of acid–base equilibrium conditions on groundwater chemistry.

Factor scores associated to each well are determined and plotted in order to illustrate the spatial characteristics of shallow waters quality in the study area (Fig. 10(a) and (b)). The spatial distribution of factor scores does not show clear trends. It is related to the effect of the natural processes and the influence of anthropogenic pollution. The spatial distribution of the F1 scores (Fig. 10(a)) indicates that most of the area is characterized by high values especially on the shorelines of Chott Djerid or downstream the study area. This is related to the influence of halite and gypsum features and dissolution of evaporite rocks. In fact, the shoreline of Chott Djerid is influenced by the accumulation of drainage waters

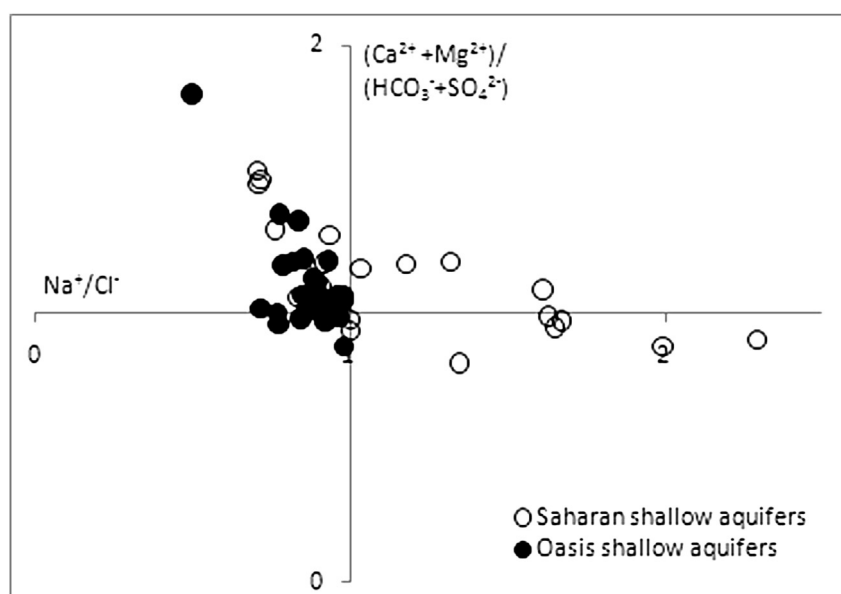


Fig. 7. Relationships between major elements of $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$ and Na^+/Cl^-

Table 2
Correlation matrix for chemical parameters.

	pH	Cl	NO ₃	SO ₄	HCO ₃	Na	K	Mg	Ca	TDS
pH	1									
Cl	−0.36	1								
NO ₃	0.27	−0.19	1							
SO ₄	−0.52	0.76	−0.15	1						
HCO ₃	−0.72	0.33	−0.32	0.52	1					
Na	−0.41	0.97	−0.11	0.80	0.34	1				
K	−0.17	0.41	0.26	0.59	0.10	0.53	1			
Mg	−0.52	0.83	−0.26	0.89	0.59	0.81	0.43	1		
Ca	−0.40	0.78	−0.17	0.89	0.42	0.75	0.38	0.77	1	
TDS	−0.50	0.93	−0.15	0.93	0.48	0.94	0.53	0.92	0.88	1

downstream of the oasis and hence the infiltration of these superficial salty waters into the shallow aquifers could significantly contribute to the groundwater mineralization (Kraiem et al., 2012).

Fig. 10(b) shows the spatial distribution of F2 scores. It demonstrates that most of the water samples were moderately affected by this factor. Moreover, this factor indicated the effect of the carbonates dissolution which mainly characterizes the oasis shallow aquifers situated in the western part of Chott Djerid. Besides F2 does not depict the NO₃[−] concentrations which elucidates their anthropogenic origin.

4.3. Origins and spatial distribution of nitrates

Nitrate contents were plotted towards TDS (Fig. 11(a)), showing that the oasis shallow aquifers were depleted in nitrate contents except for samples no. 3 with 82.8 mg NO₃[−]/l. Nitrate contents in Saharan shallow aquifers are lower than 100 mg/l except for samples no. 38 and 32 with 558 mg/l and 422.8 mg/l, respectively. We shows a relative correlation

Table 3

Loading of the components obtained from principal component analysis, with 2 factors: Eigenvalue derived by factor analysis and cumulative % explained by factors.

	Factor 1	Factor 2
pH	−0.41	−0.68
Cl	0.90	0.12
NO ₃	0.00	−0.75
SO ₄	0.93	0.21
HCO ₃	0.38	0.75
Na	0.93	0.07
K	0.68	−0.38
Mg	0.87	0.34
Ca	0.86	0.20
TDS	0.97	0.19
Eigenvalue	6.19	1.57
Cumulative Eigenvalue	6.19	7.75
% Total variance	61.89	15.65
Cumulative %	61.89	77.54

between TDS and NO₃[−] contents below 100 mg/l, indicating that nitrate also contributes to the mineralization of these waters mainly located along the Dahar piedmont.

Indeed, several hypotheses could be proposed about the origin of nitrate in shallow waters: Huang et al. (2010) and Darwish et al. (2011) found that nitrates could be explained by ex situ contamination of shallow aquifers by fertilizers, manure or animal wastes, septic contamination (Withers et al., 2012). In situ complex hydrochemical processes including nitrification and denitrification could be adopted as potential sources of nitrates (Sliva and Williams, 2001; Andrade and Stiger, 2009).

Most of the nitrate enriched samples were located in the Sahara without any agricultural activities. Furthermore, the absence of correlation between NO₃[−] and Ca²⁺ ions (Fig. 11(b)) indicates that the origin of the nitrates could not be linked to agriculture practices. However, some exceptions have been

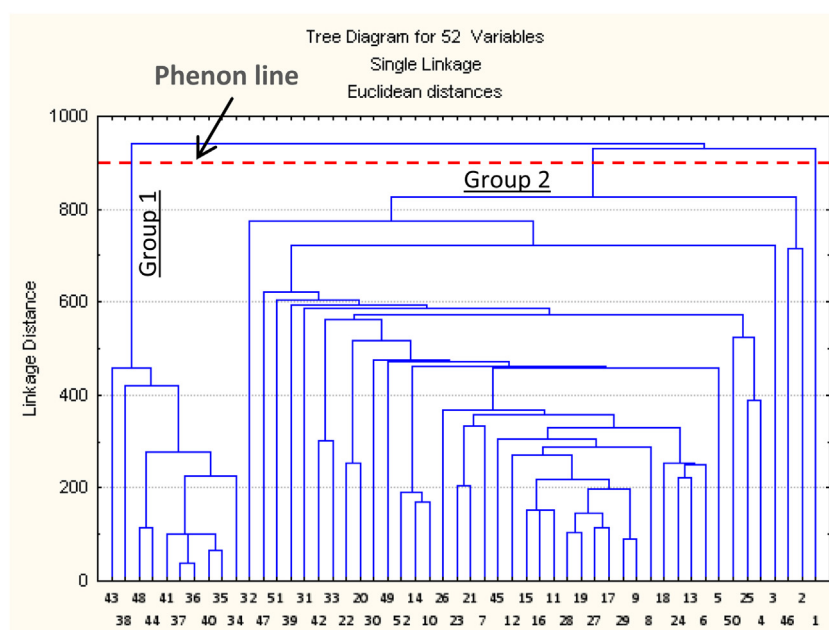


Fig. 8. Results of the hierarchical cluster analysis shown by a dendrogram.

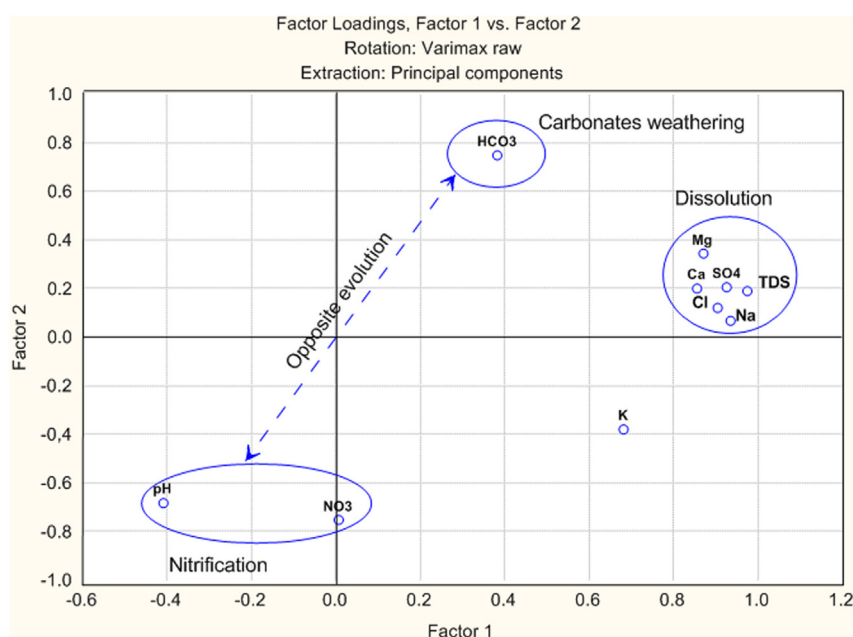


Fig. 9. Plot of factor loadings for the first two factors.

noted during field trips. Sample no. 3 with 82 mg NO_3/l , situated in an oasis close to a farming house, is likely to be contaminated by a septic tank. Moreover, some water points are mainly used by nomadic tribes to provide drinking water to their livestock. Due to high mobility of nitrate in sandy soils, these waters could be contaminated by leaking of nitrates (Nolan, 1999) after rainy periods.

High nitrate contents found under bare soils are related to aerobic conditions and high pH values indicating the role of acid base equilibrium conditions (Thayalakumaran et al., 2008; Stumm and Morgan, 1996).

4.4. Suitability of water for drinking and agricultural use

According to the hydrochemical and the statistical investigations, we can determine the suitability of the water for different uses. This method could be applied to arid and semi

arid climate subjected to natural and anthropogenic constraints. It is used to determine the vulnerability of waters based on the availability of data and the facility of the analysis with appropriate spatial distributions. However, it is difficult to distinguish between the natural mineralization and the induced mineralization (irrigation return flow and contamination).

4.4.1. Drinking purpose

According to WHO (2008), no standards have been created for TDS, chloride, sodium, hardness, sulfates and potassium. The only available standard that was established is based on taste. Generally, waters with TDS lower than 1000 mg/l are acceptable for consumers. Chloride however can have an undesirable taste at a concentration higher than 250 mg/l. Yet, drinking water with a chloride concentration higher than 250 mg/l and a limit of 600 mg/l is sometimes acceptable. The

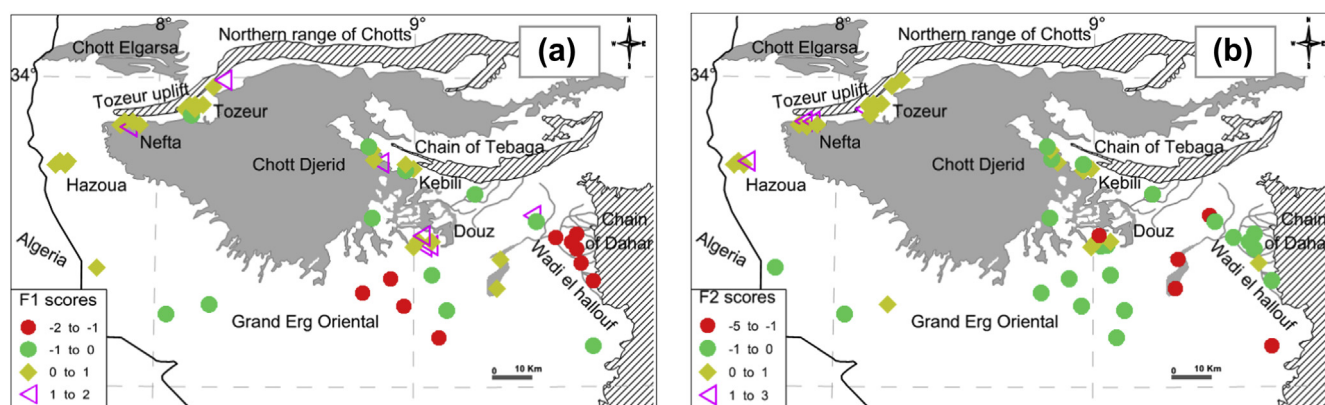


Fig. 10. Spatial distribution of the F1 factor scores (a) and F2 factor scores (b).

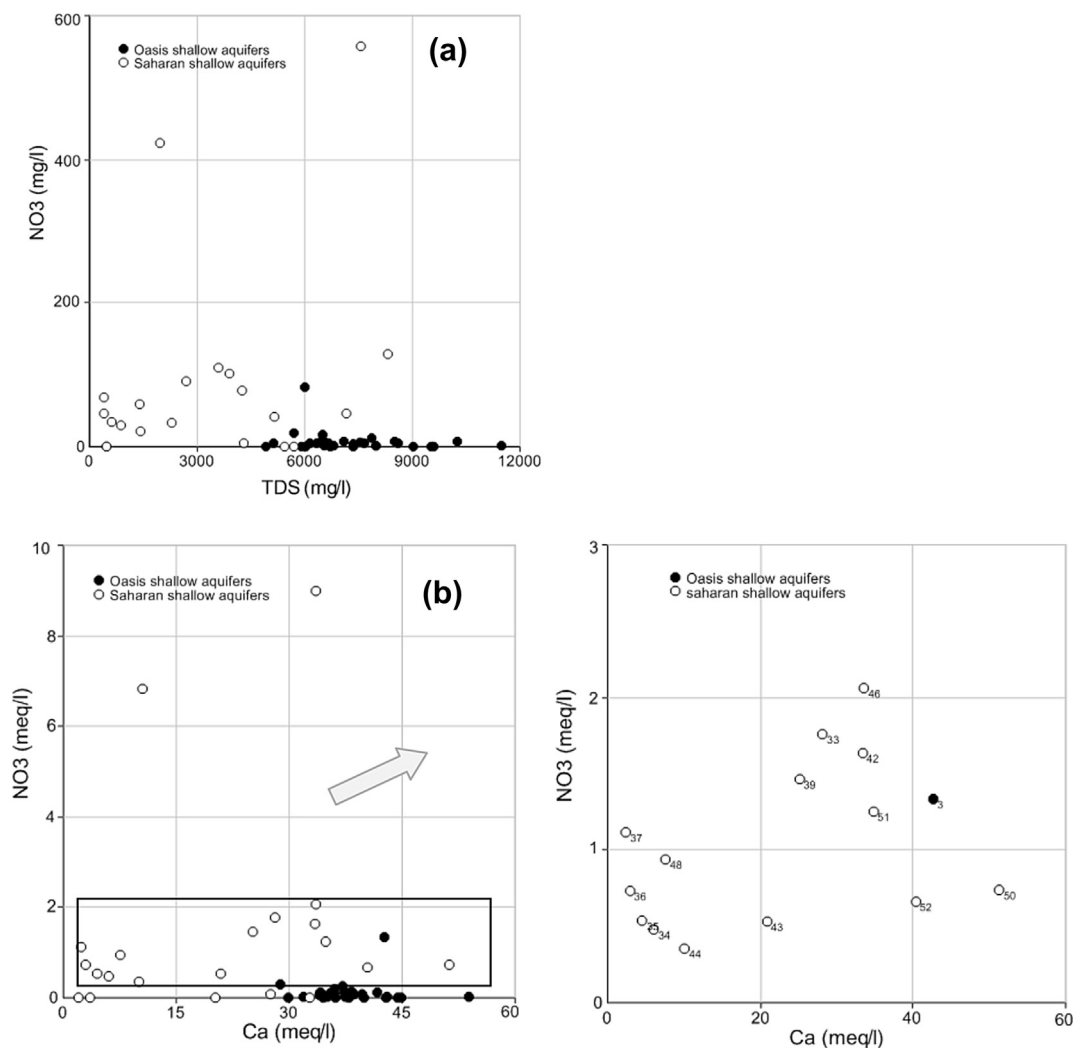


Fig. 11. TDS vs. NO_3^- (a) and NO_3^- vs. Ca^{2+} (b) relationships.

sodium standard concentration is less than 200 mg/l. For calcium, the taste is between 100 and 300 mg/l and for magnesium is lower than this limit. So, water must have a hardness that doesn't exceed 500 mg/l. Sulfates should be detected at concentrations of less than 500 mg/l. For nitrates, the standard of 50 mg/l is essentially based on health effects.

According to the WHO (2008) drinking water standard, the chemical composition for group 1 waters demonstrates that, despite the acceptable concentrations in major cations and anions, samples no. 34, 35 and 37 have high nitrate contents that could have adverse consequences on health (Suthar et al., 2009). It may be toxic for infants and may result in stomach cancer for others (Spalding and Exner, 1993).

4.4.2. Irrigation purpose

To determine the suitability of water for irrigation use, the sodium absorption ratio (SAR) has been plotted with the electrical conductivity (EC) measurements on the classical U.S. Salinity Laboratory Classification diagram (Wilcox, 1955). The SAR is an important parameter for determining the suitability of irrigation water because it is a measure of

alkali/sodium hazard for crops. It is defined as a function of Na^+ by the average and the square root of the sum of Ca^{2+} and Mg^{2+} ; $\text{SAR} = [\text{Na}^+]/([[\text{Ca}^{2+}] + [\text{Mg}^{2+}]]/2)^{1/2}$ where $[i]$ is the concentration of referred ion in mmol/l. The critical value is reached when the $\text{SAR} = 10$ (Appelo and Postma, 1994). In fact, soil structure problems occur when Na^+ ions reach a limit of 15% of exchangeable cations and when the ionic strength of the solution is less than 0.015 (Appelo and Postma, 1994).

The analytical data plotted on the U.S. salinity diagram (Fig. 12) illustrates that about 12% of samples fall in the $\text{C}_2\text{--S}_1$ (samples no. 36, 37 and 41) and $\text{C}_3\text{--S}_1$ (samples no. 35, 40, 34) zones indicating waters with respectively medium to high salinity and low SAR. These water samples have good water conditions for irrigation purposes. One sample falls in the $\text{C}_4\text{--S}_1$ type (samples no. 39) indicating water with very high salinity and low sodium adsorption ratio. This could be suitable for plants having good salt tolerance and restricts their suitability for irrigation especially in soils with restricted drainage. About twelve samples fall in the $\text{C}_4\text{--S}_2$ class (samples no. 43, 44, 48, 23, 13, 42, 14, 10, 52, 3, 54 and 27) indicating water with very high salinity and medium sodium adsorption ratio. They

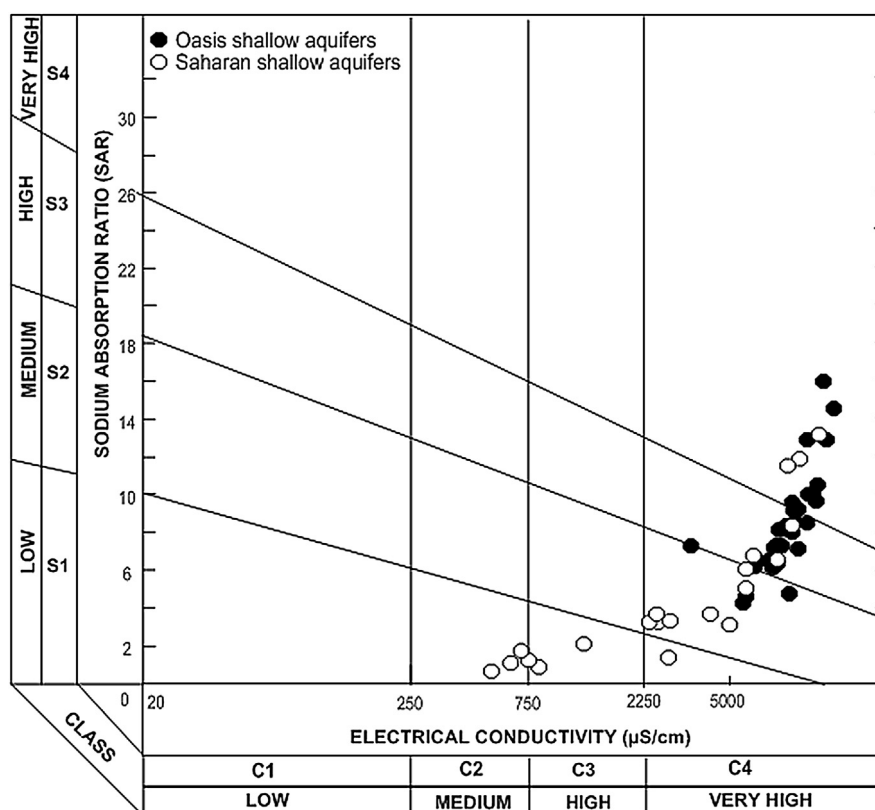


Fig. 12. samples plotted on the U.S. salinity laboratory diagram.

were considered with moderate SAR and can be used to irrigate salt tolerant and semi tolerant crops under favorable drainage conditions. Finally, we show that the remaining samples with about 40% and 23% fall in the C_4-S_3 and C_4-S_4 classes, respectively, indicating waters with very high salinity and high to very high SAR. These water samples, considered as low quality, were found to be unsuitable for irrigation; they should not be used for irrigation on clay soils of low permeability.

5. Conclusions

Based on hydrogeological characteristics and geographical distributions, shallow aquifers in southwestern Tunisia can be classified into two groups: (1) the oasis and (2) the Saharan shallow aquifers. Our results showed a Ca-SO_4 water type for Kebili oasis shallow aquifers and a Na-Ca-Cl water type for the Douz and Djerid oasis shallow aquifers. Saharan shallow aquifers also showed two different water types: a $\text{Ca-HCO}_3\text{-NO}_3$ facies representative of fresh shallow waters ($\text{TDS} < 2.2 \text{ g/l}$) located near the Dahar piedmont and a mixed facies ($\text{Na-Ca-SO}_4\text{-Cl}$), representative of the remaining Saharan shallow waters.

Major elements distributions suggested that the dissolution of halite and gypsum in evaporites within the Mio-Plio-Quaternary deposits was the main source of these ions in groundwater. Molar ratios of $(\text{Na}^+/\text{Cl}^-)$, $(\text{Mg}^{2+}/\text{Ca}^{2+})$ and $(\text{SO}_4^{2-}/\text{Cl}^-)$ vs. Cl^- , observed in the wells of the Dahar chain piedmont, were >1 , which may indicate the occurrence of cation exchange reactions through the release of Na^+ into the

water simultaneously with the removal of Ca^{2+} . The existence of such an exchange is confirmed by the balance between the Na^+/Cl^- and $(\text{Ca}^{2+} + \text{Mg}^{2+})/(\text{HCO}_3^- + \text{SO}_4^{2-})$.

Both hydrogeochemical and statistical analyses showed good agreement. Using the cluster analysis, shallow waters can be classified into two groups with 2.2 g/l TDS as a limit. The factor analysis indicated two main factors controlling the mineralization: (1) factor 1 marked by strong concentrations of major ions and TDS values. The concentrations of these elements contribute to the mineralization by dissolution of evaporite minerals; (2) factor 2 marked by the opposite evolution of HCO_3^- and (NO_3^-) , pH). This factor reflects the effect of carbonates dissolution and nitrates pollution affecting several wells of the Saharan shallow aquifers. This pollution is of anthropogenic origin, mainly related to the infiltration of pasture needs and/or reduction of atmospheric nitrites.

Based on the U.S. salinity laboratory diagram, we concluded that the waters situated in the Dahar piedmont and the south west of Douz region could be used for irrigation. In contrast, waters of other areas were found to be unsuitable because of their major risk on water use and soil vulnerability.

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