

Hydro-geochemical processes in the Complexe Terminal aquifer of southern Tunisia: An integrated investigation based on geochemical and multivariate statistical methods



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ABSTRACT

Hydrochemical data from a total of 104 groundwater samples were used to investigate the main factors and mechanisms that control the chemistry of groundwaters in the Complexe Terminal (CT) aquifer of Chott region in southern Tunisia. Multivariate statistical techniques combining Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) were applied to the dataset of 12 physicochemical parameters (i.e. pH, T° , depth, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , HCO_3^- , NO_3^- , Cl^- , SO_4^{2-} , and TDS). The HCA using Ward's method and squared Euclidean distance classified the parameters into four clusters based on their dissimilarities. The application of PCA resulted in two factors explaining 64.25% variance. Geochemical methods combined with HCA and PCA confirm that groundwater chemistry is not controlled by the different lithological facies of the aquifer, but by the presence of evaporates randomly distributed in the basin.

Although stable isotope data (^2H and ^{18}O) of some groundwater are consistent with a slight modern recharge, CT groundwaters are mostly depleted bearing witness to the recharge of the aquifer system occurred under different climatic conditions than present. The stable isotopic composition of these paleo-waters which all lie to the right of the local meteoric water line also indicates more pronounced evaporation of rainfall during the recharge process than during present-day conditions.

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1. Introduction

In many arid basins, groundwater is the only available resource to sustain economic development and ensure water security of local communities. Southern Tunisia regions are good illustrations of such areas where natural and anthropogenic stress highly affect water resources inducing important disruptions of groundwater

over large areas. Due to low precipitation (150 mm year^{-1}) and scarcity of permanent surface water, the increasing water demands for domestic, touristic, agricultural and industrial usages in this region is mainly supported by groundwater abstraction from the North Western Sahara Aquifer System (NWSAS). This system extending between Tunisia, Algeria and Libya is known as one of the largest groundwater systems of the world and consists of two main aquifers, the Complexe Terminal (CT) and the Continental Intercalaire (CI) aquifers which contain large reserves estimated at $31,000 \times 10^9 \text{ m}^3$ (ERESS, 1972; Mamou, 1990; OSS, 2003). Despite the importance of this resource, basic information on the hydrological parameters and the geochemical behavior of these aquifer systems are often lacking to assess its sustainability.

The present paper focuses on the Tunisian part of the CT aquifer whose sources springing up in the oasis are known since antiquity. Nowadays, the overexploitation of the CT aquifer has led to a general piezometric decline resulting in drying up of most springs as

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well as groundwater quality degradation (OSS, 2003; Zammouri et al., 2009). Shallow aquifers of this arid area have mostly high salinities and are not of adequate quality for human uses. This quality degradation that had been mainly related to agriculture contamination and/or irrigation return flow enhances the risk of degradation of the underlying CT aquifer by direct infiltration (Zammouri et al., 2009).

Identification of hydro-geochemical processes affecting groundwater quality in the CT aquifer would contribute to the elaboration of a sustainable water resource management program which will aim to maintain the balance between freshwater availability and human needs. In particular, processes controlling high mineralization of the CT waters observed in some points have to be identified and explained in relation with the intensive agriculture practices in this area.

Previous investigations on groundwater quality based on chemical and isotopic fingerprints have highlighted the role of evaporation, water–rock interaction and flow of saline groundwater (Kamel et al., 2007; Kamel, 2011; Zammouri et al., 2009; Abid et al., 2011). However, these studies have been carried out on some limited parts of the basin. The lack of systematic hydro-geochemical studies conducted on the whole Tunisian part of the CT considered as a single water entity has restricted the knowledge of spatial variation of groundwater quality and therefore the assessment of main mechanisms controlling the groundwater chemistry.

The objective of this study is to investigate the entire basin where the CT aquifer is exploited in order to refine the hydrodynamic continuity inside this aquifer and to constrain dominant hydro-geochemical processes controlling the variability of groundwater chemistry. These processes were investigated using integrated multivariate statistical methods applied to physico-chemical data and supported by stable isotopes (^{18}O , ^2H) data.

These methods were employed (1) to determine dominant geochemical processes taking place in the system, (2) to identify homogeneous water groups with similar chemical characteristics, (3) to characterize chemical and isotopic fingerprints of groundwater, (4) to determine sources and mechanisms of groundwater recharge and (5) to elucidate the mixing relationships between the different aquifer horizons.

2. Geological and hydrogeological settings

The investigated area, located in southern Tunisia, is limited East by the Tebaga-Kebili and Dahar mountains, north by the Metlaoui highlands, west by the Algerian frontier and south by the Tunisian part of the Great Oriental Erg. This area includes two large hypersaline depressions, locally called Chott El Gharsa and Chott Djerid, around which are dispersed oasis and cultivated fields (Fig. 1). These two hypersaline depressions are the result of a pronounced subsidence and are separated by the northern uplands of the Chotts and by the Drâa Djerid anticline also known as “Tozeur uplift” (Mamou, 1990).

These geological features are due to a set of NW/SE, E/W and NE/SW faults and associated fractures (Zargouni et al., 1985; Zouaghi et al., 2005). Thus, the tectonic activity largely controls the topography, surface drainage pattern, and possibly the groundwater flow. High heterogeneity of geological formations in term of thickness and lithofacies is likely related to the complex tectonic evolution of the area (Zargouni et al., 1985; Bouaziz, 1995; Gabtni et al., 2009).

The basin is mainly composed of Quaternary, Tertiary and Late to Early Cretaceous deposits (Fig. 2). Plio-Quaternary layers, known as the “Segui Formation”, consist of a succession of gypseous silty to sandy deposits which constitute the upper shallow aquifers (Castany, 1954; Burollet, 1956; Zargouni et al., 1985; Tlig et al.,

1991). These shallow aquifers are separated from deeper levels by Pliocene clay layers. Miocene continental sands of the “Beglia Formation” constitute with the Late Cretaceous carbonates the two main water-bearing formations of the CT aquifer (Burollet, 1956; Mannai-Tayeche, 2009). Petroleum well data provided by ETAP (Entreprise Tunisienne des Activités Pétrolières) show that the “Beglia” formation is constituted by sandstone and claystone alternation interbedded in some places with gypsum, anhydrite and calcareous marl. The Late Cretaceous formations are made up of a fractured limestone interbedded with layers of dolomite, clay and marl.

In the Late Cretaceous deposits, water is contained in two main reservoirs of the Senonian and Turonian formations. The Miocene and Senonian aquifers are isolated from each other by the Paleocene and Eocene deposits, which have been recognized in Hazoua, Nefta and Tozeur with a thickness less than 300 m. Eastward of Tozeur, Miocene sequences overlie unconformably the Senonian strata (Chaâbani, 1995; Kamel, 2007). The Turonian aquifer is separated from the overlying Senonian layers by Coniacian strata which are represented by clays and marls with limestone and gypsum intercalations. Early Cretaceous deposits, characterized by dolomites, marls, clays and sandstones, constitute the deeper Continental Intercalaire (CI) aquifer. The CT and the CI aquifers are separated by the Late Albian–Cenomanian formations constituted by marls, clays and dolomitic limestone beds.

The CT multi-layered aquifer is heavily exploited both in the Nefzaoua basin around the Kebili city and in the Djerid basin which includes Redjime Mâatoug, Tozeur and the Chott El Gharsa Plain. The CT is contained in Senonian and Turonian carbonate formations in the Nefzaoua basin while the reservoir layers are in Mio-pliocene sands in the Djerid basin.

In the Nefzaoua basin, groundwater flows broadly along a unique SE to NW direction, from the Dahar uplands toward the Chott Djerid depression. By contrast, several flow lines have been identified in the Djerid basin converging toward the Chott Djerid and Chott El Gharsa depressions from the Metlaoui highlands, the northern uplands of the Chotts and from the Algerian–Tunisian Great Oriental Erg. Some secondary flow lines coming from the Tozeur uplift could also be noticed (Fig. 3).

The CT aquifer is confined over most of the basin, except in the south-eastern part of the Nefzaoua, where the carbonate aquifer formations outcrop, especially in the Dahar uplands and the region of Douz-Jemna. These outcrops constitute one of the recharge areas of the aquifer. Furthermore, Miocene sands in Djerid basin are unconfined at many localities (Kriz-El Hamma-Degache area) and outcrop along the western extremity of the northern uplands of the Chotts and along the Tozeur uplift that also constitute some eventual recharge areas.

3. Groundwater sampling and methods

The sampling network covers the entire basin. We paid special attention to sample the different lithological formations, at different depths, and to cover the recharge and discharge zones of the multi-layer aquifer. Thus, the data can be assumed as representative of most of the geochemical processes that take place in the CT aquifer.

A total of 104 groundwater samples were collected from the main hydrogeological units of the survey area during March 2010 and March 2011 (Fig. 1). Borehole depths range typically between 30 and 1100 m. Forty-one (41) boreholes have been sampled in the Nefzaoua basin; three (3) from the Turonian levels (#T1–#T3) and thirty-eight (38) from the Senonian limestone ones (#S20–#S57). Besides, sixty-three (63) boreholes have been sampled from the sandy Mio-Pliocene levels in the Djerid basin; sixteen (16) at Redjime Mâatoug (#MR4–#MR19), thirty-four (34) at Tozeur

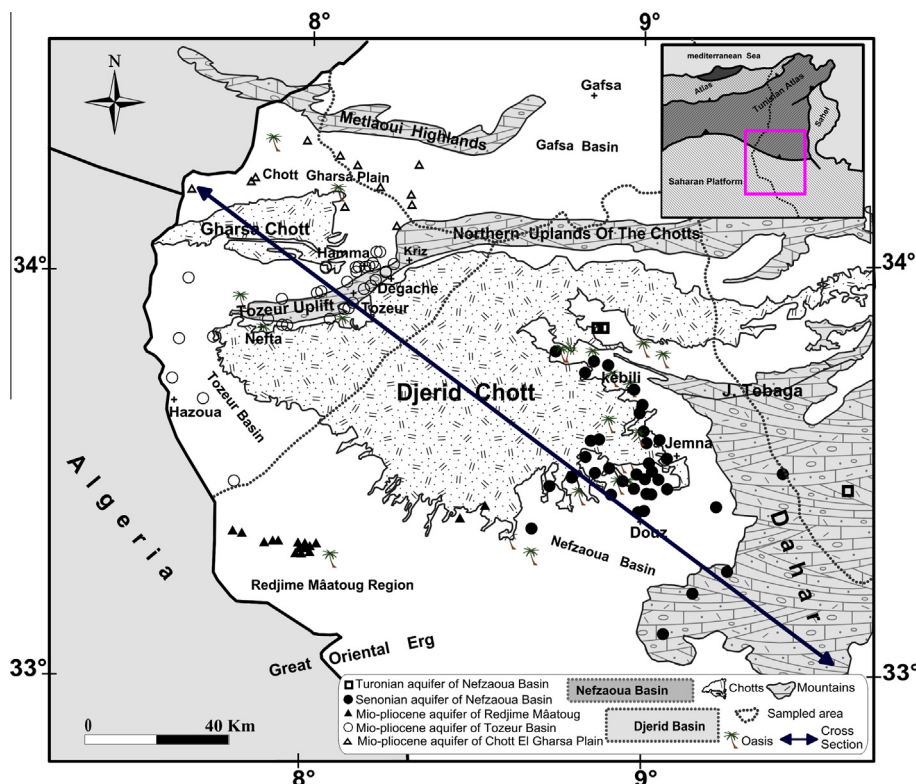


Fig. 1. Map of the study area showing sample locations.

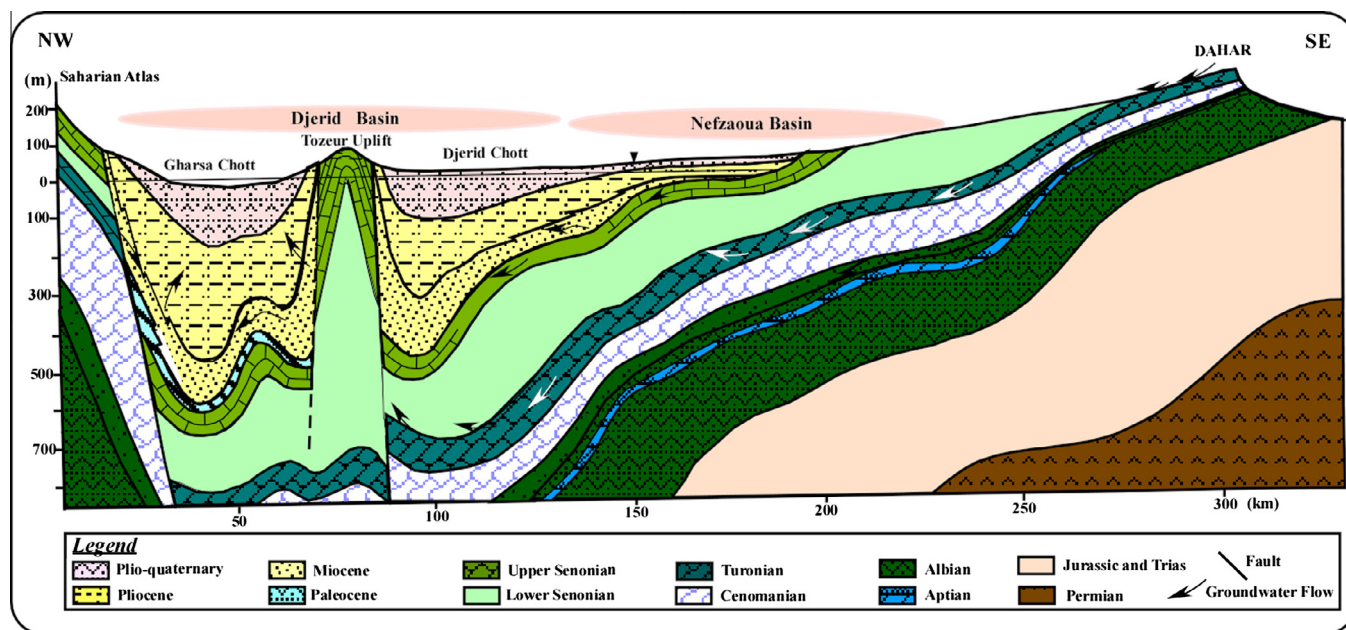


Fig. 2. Hydrogeological cross section of CT aquifers.

(#MT58–#MT91) and thirteen (13) at Chott El Gharsa plain (#MC92–#MC104). All samples were collected from currently exploited wells in order to ensure that water is representative of actual aquifer conditions.

Samples were collected in polyethylene bottles previously washed with diluted nitric acid and rinsed with sample groundwater prior to sampling. All samples were filtered with a 0.45 μm cartridge filter and cation samples were preserved with nitric acid

(HNO_3) to prevent precipitation. Stable isotope samples were collected in glass bottles with airtight caps to prevent leakage or evaporation.

Temperature (T°), pH and electrical conductivity (EC) were measured *in situ*, using a HI 9828 Multiparameter equipment. All samples were analyzed for main chemical parameters using standard methods. Analyses of cations (Ca^{2+} , Mg^{2+} , Na^+ and K^+) and anions (Cl^- , SO_4^{2-} , NO_3^-) were carried out in the Laboratory of

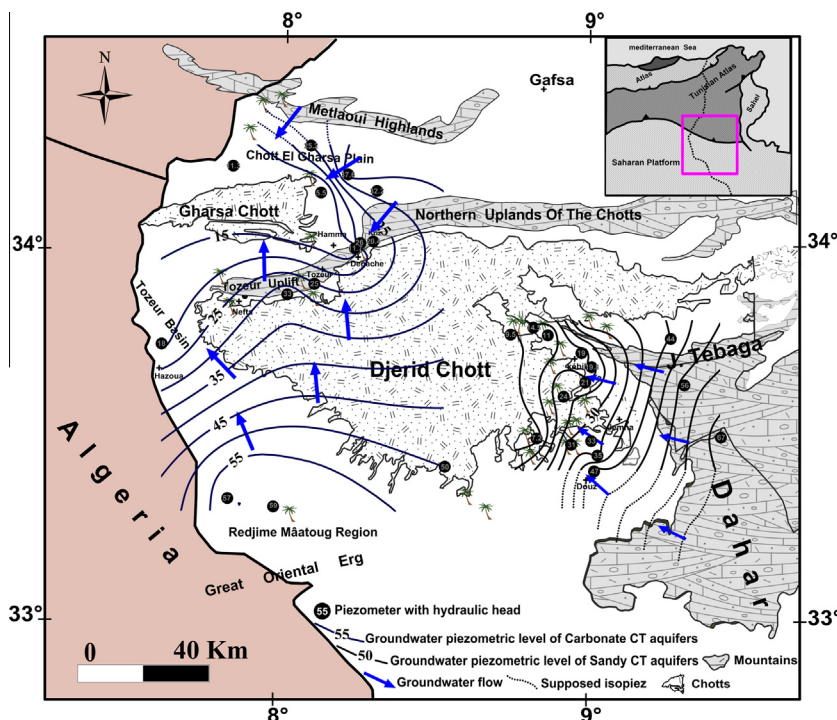


Fig. 3. Map of groundwater piezometric level of CT aquifers.

Radio-Analyses and Environment of National School of Engineers of Sfax (Tunisia) with Liquid-Ion Chromatography (HPLC) on a WatersTM 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 overall detection limit for ions was 0.04 mg/l. The total alkalinity (as HCO_3^-) was determined by titration with 0.1 HCl against methyl orange and bromocresol green indicators. The reliability of the chemical data was assessed by checking ion balance. Calculated charge balance errors are found to be less than $\pm 5\%$ which is an acceptable uncertainty for the purpose of this study.

Stable isotope composition of water samples ($\delta^{18}\text{O}$, $\delta^2\text{H}$) was determined at the Laboratory of Radio-Analyses and Environment by Laser spectrometry measurement. The results are expressed as relative deviations δ (in per mil) from the Vienna Standard Mean Ocean Water (VSMOW). The analytical precision of stable isotope analyses (1σ) was in the order of 0.1‰ for $\delta^{18}\text{O}$ and 1‰ for $\delta^2\text{H}$.

Evaluation of the groundwater data was carried out by statistical methods, and afterward, geochemical and isotopic methods were made to establish the processes controlling the groundwater chemistry. The concentrations of major ions in groundwater may be correlated based on underlying physical and chemical processes. Hierarchical Cluster analysis (HCA) was used to identify natural groupings in a dataset according to chemical dissimilarity of the samples (Farnham et al., 2000; Kuells et al., 2000; Alberto et al., 2001; Güler and Thyne, 2004; Thyne et al., 2004). This hierarchical clustering was developed using a combination of the Ward's linkage method (Ward, 1963) and squared Euclidean distances as a measure of dissimilarity. Finally, it produces a graphical representation or dendrogram of individual groups, containing samples with close values of parameters. The HCA was completed by a PCA. This technique is used to distinguish different groups of geochemical variables according to their degree of co-variation. The aim of PCA is to associate a large number of observed variables into a smaller number of factors (components) that can be more readily interpreted as these underlying processes (Mathes and

Rasmussen, 2006; Lorite-Herrera et al., 2009). Both HCA and PCA were performed using XLSTAT statistical software.

The evolution of geochemical processes in groundwater depends on the equilibrium between mineral phases and water and is commonly discussed by saturation indices. A positive value of saturation indices computed with respect to solid phase, following Garrels and Christ (1965), indicates an oversaturated state. In our case, saturation indices have been calculated from most common minerals encountered in the aquifer formation, i.e. calcite, dolomite, halite and gypsum using DIAGRAM software (Smiler, 2004).

Moreover, stable isotopes (deuterium and oxygen-18) have been used as an integral component of hydrogeological and geochemical methods in order to identify possible recharge processes and mixing within aquifer systems (Fontes, 1980; Rozanski, 1985; Edmunds et al., 1992; Clark and Fritz, 1997).

4. Results

Chemical analyses and field measurements for the 104 groundwater samples are summarized in Table 1. Temperature varies between 18 and 49 °C, along a normal geothermal gradient of 30 °C/km (Ben Dhia, 1987). pH ranges from 7.1 to 8.8, and EC values from 1090 $\mu\text{S}/\text{cm}$ to 9908 $\mu\text{S}/\text{cm}$ with a mean of 4145 $\mu\text{S}/\text{cm}$ (i.e. TDS from ca. 630 to 7050 mg/l).

The ionic composition is dominated by Ca^{2+} (68–941.3 mg/l), Na^+ (77.9–1357.2 mg/l), Cl^- (135.4–2775.3 mg/l) and SO_4^{2-} (141.6–2307.7 mg/l) (Tables 1 and 2). By contrast, concentrations in Mg^{2+} (25.3–366.4 mg/l) and K^+ (less than 73.5 mg/l) are relatively lower.

High correlations are observed between sodium and chloride ions ($r = 0.95$) as well as between calcium and sulfate ($r = 0.72$), and magnesium and sulfate ($r = 0.75$). By contrast, bicarbonate is not correlated with either EC ($r = 0.08$) or Ca^{2+} ($r = 0.13$) (Table 3).

In this study, twelve physico-chemical variables (pH, T° , depth, Na^+ , K^+ , Ca^{2+} , Mg^{2+} , alkalinity, NO_3^- , Cl^- , SO_4^{2-} and EC) in 104

Table 1
Physico-chemical results (ionic contents in mg/l, depth in m, T° in °C) and stable isotope contents of the water sample analysis of CT groundwater.

Wells	Aquifer	Basin	Depth	pH	T°	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	TDS	δ ¹⁸ O VSMOW	δ ² H VSMOW
T1	Turonian	Nefzaoua	422.8	7.40	26.70	603.77	37.62	1111.22	122.00	366.35	20.40	129.75	302.90	2718.02	-7.2	-54.54
T2	Turonian	Nefzaoua	33.0	7.60	26.10	753.72	21.52	1448.44	140.30	443.28	19.80	154.00	430.80	3411.86	-6.57	-50.48
T3	Turonian	Nefzaoua	43.60	7.25	26.10	780.52	48.04	1582.40	134.20	442.60	20.92	153.64	436.72	3599.04	-6.68	-50.39
MR4	Mio-pliocene	Redjime Maatoug	225.00	7.76	26.80	513.25	31.72	1163.75	146.40	321.42	23.97	147.62	348.47	2696.62	-4.96	-47.82
MR5	Mio-pliocene	Redjime Maatoug	180.00	7.80	26.30	521.80	35.50	1145.45	140.30	324.22	23.95	146.75	322.90	2660.87	-5.60	-49.11
MR6	Mio-pliocene	Redjime Maatoug	195.00	7.99	25.50	500.25	13.47	1189.65	65.88	303.37	23.92	113.10	308.02	2523.68	-5.13	-49.44
MR7	Mio-pliocene	Redjime Maatoug	164.30	7.88	26.10	399.54	32.26	818.64	134.20	250.56	18.24	108.68	212.30	1986.42	-4.15	-44.41
MR8	Mio-pliocene	Redjime Maatoug	118.00	8.25	22.40	254.46	15.17	305.67	122.00	155.27	14.89	51.81	110.79	1054.06	-5.64	-53.51
MR9	Mio-pliocene	Redjime Maatoug	190.00	7.76	22.70	554.82	28.20	1141.40	219.60	343.67	29.45	123.95	343.67	2784.77	-4.58	-46.71
MR10	Mio-pliocene	Redjime Maatoug	117.7	8.48	22.80	272.81	14.21	306.80	170.80	172.42	24.46	31.54	132.29	1126.04	-4.87	-45.45
MR11	Mio-pliocene	Redjime Maatoug	272.00	7.90	25.00	465.64	14.40	883.32	140.30	249.10	22.00	113.02	211.54	2099.32	-4.18	-46.18
MR12	Mio-pliocene	Redjime Maatoug	271.00	7.70	28.00	472.88	14.64	857.84	134.20	256.48	18.78	112.12	274.40	2141.34	-4.24	-44.96
MR13	Mio-pliocene	Redjime Maatoug	274.90	7.50	19.00	453.10	13.84	870.82	128.10	239.54	17.48	116.08	284.36	2123.32	-4.54	-46.71
MR14	Mio-pliocene	Redjime Maatoug	232.00	8.00	25.00	457.90	13.16	793.62	140.30	249.62	20.18	104.86	213.42	1993.06	-4.33	-45.84
MR15	Mio-pliocene	Redjime Maatoug	278.30	7.50	27.00	488.12	12.97	924.07	134.20	254.60	23.47	121.72	239.37	2198.55	-4.09	-47.07
MR16	Mio-pliocene	Redjime Maatoug	279.10	7.80	26.00	504.32	11.85	1124.07	140.30	322.72	23.82	145.00	349.25	2621.35	-5.21	-52.34
MR17	Mio-pliocene	Redjime Maatoug	171.00	7.80	25.00	479.52	18.10	755.62	140.30	259.86	22.02	108.22	208.38	1992.02	-4.03	-46.66
MR18	Mio-pliocene	Redjime Maatoug	280.00	7.90	27.00	533.85	14.90	1089.40	134.20	319.10	28.67	131.17	313.15	2564.45	-5.20	-50.95
MR19	Mio-pliocene	Redjime Maatoug	285.40	7.30	25.00	563.75	16.02	1243.00	140.30	310.22	23.65	138.07	341.50	2776.52	-5.92	-51.88
S20	Senonian	Nefzaoua	72.00	8.05	22.90	404.30	23.86	402.90	115.90	209.96	11.20	72.04	193.66	1451.82	-6.16	-51.72
S21	Senonian	Nefzaoua	37.00	8.10	24.00	999.27	53.15	736.20	134.20	544.12	25.20	126.05	227.20	2845.40	-5.88	-46.24
S22	Senonian	Nefzaoua	63.50	7.98	24.70	472.18	32.16	505.02	122.00	211.28	10.66	68.26	175.70	1597.26	-6.19	-53.89
S23	Senonian	Nefzaoua	102.00	8.00	25.70	491.46	45.02	519.24	134.20	247.02	14.72	81.18	185.28	1718.12	-6.14	-50.90
S24	Senonian	Nefzaoua	134.58	8.29	18.10	639.64	29.94	376.72	54.90	239.60	12.18	75.20	175.34	1609.52	-6.13	-51.11
S25	Senonian	Nefzaoua	17.50	8.00	25.00	613.67	98.52	990.62	115.90	374.40	15.55	93.57	329.32	2631.57	-6.01	-49.33
S26	Senonian	Nefzaoua	91.00	8.08	25.60	425.26	14.76	491.32	122.00	223.44	12.02	78.34	172.28	1557.42	-6.24	-50.68
S27	Senonian	Nefzaoua	59.00	8.16	24.60	393.19	33.04	343.74	128.10	205.98	13.44	62.15	139.70	1319.34	-6.17	-48.69
S28	Senonian	Nefzaoua	35.60	7.49	26.00	2211.84	47.20	2001.12	128.10	1357.28	73.52	366.40	459.12	6662.58	-5.13	-40.34
S29	Senonian	Nefzaoua	49.00	7.90	22.00	135.40	59.74	141.57	109.80	77.96	7.25	25.33	74.04	631.12	-5.48	-41.57
S30	Senonian	Nefzaoua	88.50	8.09	24.80	407.56	34.00	477.04	109.80	222.12	12.96	65.00	146.80	1493.28	-4.69	-46.77
S31	Senonian	Nefzaoua	52.00	7.14	23.50	1947.8	24.20	1241.05	122.00	975.50	32.20	244.35	521.35	5108.45	-5.84	-47.26
S32	Senonian	Nefzaoua	92.00	7.90	25.50	780.575	17.60	1230.87	160.30	442.95	26.37	123.80	352.65	3135.12	-6.07	-48.82
S33	Senonian	Nefzaoua	109.00	8.04	24.70	511.06	45.18	388.40	122.00	243.46	16.74	92.20	178.00	1597.04	-6.14	-48.63
S34	Senonian	Nefzaoua	49.00	7.50	22.80	1121.75	23.02	699.30	115.90	510.20	46.32	147.17	359.30	3022.97	-5.80	-46.19
S35	Senonian	Nefzaoua	60.00	8.01	24.10	596.24	28.84	448.78	109.80	289.12	15.28	77.38	177.06	1754.50	-5.45	-45.79
S36	Senonian	Nefzaoua	48.00	8.11	25.00	1274.56	38.80	675.60	115.90	611.72	21.64	142.12	294.36	3174.70	-5.94	-44.77
S37	Senonian	Nefzaoua	58.00	7.74	24.90	942.88	29.48	1169.60	134.20	521.48	23.04	167.16	360.96	3360.80	-6.16	-49.52
S38	Senonian	Nefzaoua	94.00	8.06	26.50	445.10	32.02	707.86	122.00	265.96	12.98	94.24	194.88	1887.04	-5.71	-51.32
S39	Senonian	Nefzaoua	89.60	8.21	25.10	462.44	22.40	439.42	128.10	227.70	10.74	71.20	158.50	1520.50	-6.04	-49.89
S40	Senonian	Nefzaoua	58.00	7.78	25.70	676.92	13.44	1575.24	122.00	492.00	20.00	156.56	490.84	3583.00	-6.86	-50.99
S41	Senonian	Nefzaoua	80.00	8.00	26.00	532.95	20.47	1324.37	146.40	344.37	11.57	137.15	364.17	2881.47	-6.27	-50.93
S42	Senonian	Nefzaoua	63.20	7.80	22.60	345.79	33.53	359.13	122.00	208.35	16.13	59.12	127.10	1271.15	-5.85	-44.32
S43	Senonian	Nefzaoua	60.00	7.80	25.00	1124.72	34.56	1043.40	115.90	519.60	48.28	171.44	383.00	3440.90	-6.21	-48.85
S44	Senonian	Nefzaoua	95.00	7.00	23.10	310.97	34.79	332.54	134.20	186.94	11.16	51.50	116.31	1178.41	-5.91	-47.91
S45	Senonian	Nefzaoua	103.60	7.85	26.50	546.54	29.26	575.36	134.20	289.34	14.58	86.02	209.44	1884.74	-5.41	-51.48
S46	Senonian	Nefzaoua	52.45	7.80	24.00	770.725	36.45	787.20	128.10	373.20	23.07	121.55	310.95	2551.25	-5.69	-47.02
S47	Senonian	Nefzaoua	80.00	7.75	25.10	731.04	26.64	1634.32	115.90	476.80	16.96	153.88	476.88	3644.42	-6.49	-49.04
S48	Senonian	Nefzaoua	165.00	8.28	14.40	499.24	52.52	1249.68	134.20	356.48	19.24	146.60	296.68	2754.64	-6.81	-51.08
S49	Senonian	Nefzaoua	52.60	7.70	25.00	142.00	33.50	160.90	109.80	103.90	00.00	26.40	67.90	674.40	-5.69	-45.23
S50	Senonian	Nefzaoua	44.00	8.36	24.00	1833.37	00.00	1088.81	122.00	883.68	37.08	100.59	465.88	4319.00	-6.14	-50.50
S51	Senonian	Nefzaoua	66.00	8.82	22.60	853.78	30.14	391.96	103.70	379.01	13.84	62.13	299.58	2300.00	-5.7	-48.60
S52	Senonian	Nefzaoua	63.00	7.55	23.00	1136.00	00.00	912.00	120.00	575.00	16.00	247.00	180.00	3250.00	-5.48	-49.60
S53	Senonian	Nefzaoua	50.00	7.60	25.50	2089.84	68.43	952.49	134.20	1031.55	22.62	138.75	468.48	5276.00	-6.02	-44.66
S54	Senonian	Nefzaoua	40.10	7.90	22.00	1991.49	45.15	1037.35	109.80	1197.25	41.40	213.00	364.95	5450.00	-5.85	-44.24

(continued on next page)

Table 1 (continued)

Wells	Aquifer	Basin	Depth	pH	T°	Cl ⁻	NO ₃ ⁻	SO ₄ ²⁻	HCO ₃ ⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	TDS	δ ¹⁸ O VSMOW	δ ² H VSMOW
S55	Senonian	Nefzaoua	60.00	8.09	22.30	2733.88	00.00	1158.00	122.00	1205.85	44.19	156.93	732.24	7000.00	-6.00	-49.50
S56	Senonian	Nefzaoua	52.00	7.70	22.90	1241.24	32.48	718.60	109.80	588.96	32.76	121.68	267.60	330.00	-5.77	-46.03
S57	Senonian	Nefzaoua	47.50	7.42	22.30	2150.00	108.00	1140.60	126.00	984.70	27.3	182.80	508.10	5280.00	-5.49	-46.60
MT58	Mio-pliocene	Tozeur	75.00	7.59	30.01	395.98	19.26	515.22	116.51	181.84	4.24	80.94	237.52	1664.99	-5.99	-51.44
MT59	Mio-pliocene	Tozeur	323.00	7.30	28.54	618.95	17.10	920.40	145.18	355.15	5.25	61.40	421.10	2776.99	-4.81	-45.41
MT60	Mio-pliocene	Tozeur	367.00	7.39	31.06	636.85	18.00	993.55	143.96	384.15	00.00	116.55	299.30	2794.99	-4.85	-47.27
MT61	Mio-pliocene	Tozeur	90.00	7.71	32.14	500.00	17.02	543.44	114.07	223.18	8.26	77.02	277.08	1942.99	-6.35	-39.76
MT62	Mio-pliocene	Tozeur	112.00	7.14	31.08	602.40	00.00	1341.35	140.30	326.60	00.00	133.35	416.25	3183.99	-5.59	-44.29
MT63	Mio-pliocene	Tozeur	287.00	7.53	25.82	561.10	9.10	1135.00	161.65	321.90	29.20	127.50	405.85	3028.19	-5.15	-40.09
MT64	Mio-pliocene	Tozeur	522.00	7.20	28.41	726.00	11.15	1044.40	138.47	352.95	19.30	120.70	376.70	3068.99	-4.71	-46.56
MT65	Mio-pliocene	Tozeur	550.00	7.34	32.42	1477.30	10.55	551.85	123.83	501.50	15.20	100.45	578.50	3658.00	-5.86	-51.71
MT66	Mio-pliocene	Tozeur	500.00	7.60	34.76	485.24	15.34	464.42	115.90	196.92	6.48	32.22	316.50	1786.00	-6.09	-34.77
MT67	Mio-pliocene	Tozeur	666.00	7.29	36.19	745.70	16.85	1020.70	134.81	374.25	12.50	101.95	478.80	3139.00	-5.35	-46.18
MT68	Mio-pliocene	Tozeur	99.00	7.24	31.56	652.75	9.95	1064.45	148.84	361.70	9.60	122.05	321.65	2927.00	-5.17	-47.70
MT69	Mio-pliocene	Tozeur	98.00	7.60	31.66	606.64	14.08	468.70	108.58	297.36	15.74	74.02	165.88	1909.00	-5.52	-40.18
MT70	Mio-pliocene	Tozeur	400.00	7.43	28.40	792.30	12.38	504.28	118.34	376.36	55.46	86.00	212.70	2361.00	-5.93	-50.92
MT71	Mio-pliocene	Tozeur	279.00	7.68	29.87	539.20	14.60	560.36	126.27	294.16	14.22	72.44	175.78	1895.99	-4.37	-45.13
MT72	Mio-pliocene	Tozeur	443.00	7.42	26.75	696.60	15.60	932.40	143.35	375.50	00.00	116.30	303.75	2858.99	-4.76	-46.45
MT73	Mio-pliocene	Tozeur	64.00	7.17	33.12	2775.30	12.10	1047.50	140.30	1131.40	39.00	193.90	941.30	6290.00	-6.43	-48.48
MT74	Mio-pliocene	Tozeur	492.00	7.33	31.72	661.20	10.55	988.70	148.23	213.90	14.00	118.00	532.75	2961.00	-5.57	-39.79
MT75	Mio-pliocene	Tozeur	62.00	7.17	32.84	608.45	9.90	998.80	132.98	305.50	9.75	98.40	445.05	2907.00	-5.21	-48.09
MT76	Mio-pliocene	Tozeur	362.00	7.45	29.78	758.75	20.45	965.05	142.13	358.10	11.35	119.70	452.70	2852.99	-4.78	-45.78
MT77	Mio-pliocene	Tozeur	64.00	7.18	31.91	1964.7	28.70	794.95	128.71	823.75	29.50	150.45	487.00	4851.00	-5.64	-50.68
MT78	Mio-pliocene	Tozeur	40.00	7.16	30.37	1209.00	13.90	1518.65	132.37	606.50	20.00	179.30	480.50	4645.99	-7.05	-53.06
MT79	Mio-pliocene	Tozeur	300.00	7.55	31.53	618.24	11.18	649.50	132.98	308.18	15.30	94.54	294.58	2321.00	-5.90	-46.83
MT80	Mio-pliocene	Tozeur	496.00	7.21	31.10	668.65	8.70	1003.10	140.91	350.80	18.40	119.80	348.85	2908.00	-5.18	-38.74
MT81	Mio-pliocene	Tozeur	117.00	7.33	29.30	554.50	8.45	436.90	124.44	375.10	00.00	63.90	149.60	1712.89	-4.79	-44.89
MT82	Mio-pliocene	Tozeur	285.00	7.64	31.72	1344.70	7.96	1777.78	128.71	702.02	25.40	180.82	531.94	4980.00	-6.83	-50.06
MT83	Mio-pliocene	Tozeur	320.00	8.10	30.00	542.40	16.04	720.00	140.30	356.52	20.70	83.20	227.18	2057.99	-4.33	-42.02
MT84	Mio-pliocene	Tozeur	518.00	7.18	31.80	500.00	8.00	1120.00	134.20	307.38	19.80	122.16	310.92	2708.00	-5.01	-47.81
MT85	Mio-pliocene	Tozeur	533.00	7.85	30.00	522.00	00.00	960.00	134.20	340.08	24.00	85.08	311.54	2327.00	-4.07	-43.85
MT86	Mio-pliocene	Tozeur	603.00	7.28	30.00	472.54	18.60	818.94	134.20	295.98	18.28	99.20	239.20	2137.99	-4.18	-42.82
MT87	Mio-pliocene	Tozeur	68.00	7.20	29.00	540.00	8.00	1408.40	122.00	362.48	24.52	148.98	385.28	3335.99	-5.63	-49.64
MT88	Mio-pliocene	Tozeur	612.00	7.22	30.00	496.90	0.40	1586.34	122.00	289.26	26.80	149.84	401.08	3002.00	-6.16	-52.53
MT89	Mio-pliocene	Tozeur	65.00	8.02	28.20	598.72	15.28	1843.62	207.40	396.34	32.70	156.32	449.42	3616.99	-4.44	-45.48
MT90	Mio-pliocene	Tozeur	165.00	7.20	29.00	646.76	15.38	1135.58	128.10	369.34	27.58	136.26	307.34	2871.00	-4.34	-44.60
MT91	Mio-pliocene	Tozeur	200.00	7.80	27.00	580.00	10.54	1800.00	146.40	412.28	25.80	171.70	381.38	3521.99	-5.28	-45.02
MC92	Mio-pliocene	Chott El Gharsa	565.00	7.90	30.00	585.82	8.52	1405.77	146.40	465.36	00.00	120.15	432.85	3284.00	-7.77	-54.87
MC93	Mio-pliocene	Chott El Gharsa	600.00	7.20	30.00	635.45	0.00	1744.37	146.40	604.80	16.15	120.15	428.15	3960.99	-6.87	-51.46
MC94	Mio-pliocene	Chott El Gharsa	538.00	7.80	35.9	1881.4	0.00	1710.85	146.40	931.35	37.85	251.10	722.95	6279.00	-6.43	-49.49
MC95	Mio-pliocene	Chott El Gharsa	1052.00	8.00	49.00	749.22	7.17	1441.00	146.40	589.15	00.00	110.75	427.75	3609.99	-7.39	-56.37
MC96	Mio-pliocene	Chott El Gharsa	1174.00	8.1	39.80	805.12	4.17	1269.00	146.40	508.08	00.00	123.35	444.57	3392.00	-7.71	-52.94
MC97	Mio-pliocene	Chott El Gharsa	1064.00	7.6	45.00	748.77	6.35	1484.37	140.30	363.87	17.50	139.55	464.62	3622.00	-7.56	-57.37
MC98	Mio-pliocene	Chott El Gharsa	1164.00	7.20	42.00	1036.15	7.60	1548.90	152.50	411.30	21.45	195.85	688.70	4489.00	-7.51	-54.89
MC99	Mio-pliocene	Chott El Gharsa	1081.00	8.19	45.80	994.00	00.00	1392.00	250.00	648.00	21.00	240.00	288.00	3700.00	-5.80	-55.70
MC100	Mio-pliocene	Chott El Gharsa	846.00	7.80	41.00	1219.00	00.00	1550.00	122.00	740.00	00.00	131.00	507.20	4500.00	-7.30	-51.20
MC101	Mio-pliocene	Chott El Gharsa	660.00	7.90	30.00	852.00	00.00	1896.00	170.00	460.00	19.00	153.00	620.00	4650.00	-7.70	-51.00
MC102	Mio-pliocene	Chott El Gharsa	565.00	7.80	35.00	1775.00	00.00	2088.00	115.00	1196.00	28.00	278.00	512.00	7050.00	-7.10	-49.00
MC103	Mio-pliocene	Chott El Gharsa	345.00	7.60	33.00	567.37	00.00	2307.69	115.85	584.17	15.62	229.92	480.00	4100.00	-6.20	-39.00
MC104	Mio-pliocene	Chott El Gharsa	565	7.8	30	1078	00.00	2180	73.2	757.9	60.2	119	817.3	5170	-6.21	-41.3

Table 2
Statistical summary of the concentrations of the major parameters.

Parameters	Minimum	Maximum	Mean	Standard deviation
Depth	17.50	1174.00	257.26	270.56
pH	7.00	8.82	7.70	0.36
T°	18.00	49.00	33.50	10.33
Cl [−]	135.40	2775.30	801.06	530.79
NO ₃ [−]	00.00	108.00	21.34	18.61
SO ₄ ^{2−}	141.57	2307.69	996.65	462.84
HCO ₃ [−]	54.90	250.00	132.44	23.35
Na ⁺	77.96	1357.28	432.16	259.08
K ⁺	00.00	73.52	19.66	12.09
Mg ²⁺	25.33	366.40	124.70	55.12
Ca ²⁺	67.90	941.30	340.50	152.55
TDS	631.12	7050.00	2979.52	1333.41

samples were considered for Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA). In all following figures, samples are represented by different colors according to clusters obtained by the HCA method and by specific symbols according to the basin where they have been collected.

In following discussions, groundwaters are further subdivided into four clusters that may be ordered as C3; C4; C1; C2 according to decreasing TDS contents (Figs. 4 and 5).

Cluster C1 and C2 are composed of 41 and 44 wells, respectively. They include the majority of boreholes tapping the Tertiary and Cretaceous (Senonian and Turonian) units. The C2 cluster presents the lowest mineralization (TDS < 2500 mg/l) and lowest mean concentrations for all major elements (Fig. 5).

The majority of C2 samples, including both Senonian levels of Nefzaoua, Mio-Pliocene from the Tozeur/Degache areas and Redjime Mâatoug region, tend to be located on an inner border around Chott Djerid basin, whereas the intermediate C1 compositions (2560 < TDS < 3700 mg/l) spread as a wide outer range over Chott Gharsa, western part of Tozeur localities and on Nefzaoua basin (Fig. 6).

The C3 and C4 clusters correspond to more mineralized samples. Cluster C4 is represented by 7 samples characterized by TDS > 3700 mg/l. The last cluster (C3) includes 12 wells with higher mineralization compared to the others (TDS > 5000 mg/l). These waters come from shallow wells located either in Douz, and El Hsay in the Nefzaoua, or in the Kriz locality and in the plain of Chott El Gharsa. In the first two localities, water salinization has been already highlighted by Zammouri et al., 2009, who proposed a possible contamination of these relatively shallow CT groundwater by the shallow aquifer, marked by high salinity induced by irrigation excess and seepage of agricultural drainage basin. Consistently, several samples of this cluster are also characterized by elevated concentration of NO₃[−] (#S28: 47.2 mg/l; #S53: 68.4 mg/l; #S54: 45.1 mg/l; #S57: 108 mg/l).

Table 3
Pearson correlation for deep groundwater of CT aquifer.

Variables	Cl [−]	NO ₃ [−]	SO ₄ ^{2−}	HCO ₃ [−]	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	TDS	pH	T°	Depth
Cl [−]	1	0.08	0.33	−0.053	0.94	0.54	0.63	0.67	0.87	−0.13	0.09	−0.04
NO ₃ [−]		1	−0.30	−0.18	0.038	0.05	−0.09	−0.26	−0.12	0.16	−0.49	−0.48
SO ₄ ^{2−}			1	0.24	0.52	0.33	0.74	0.72	0.74	−0.23	0.37	0.37
HCO ₃ [−]				1	−0.01	−0.04	0.20	0.12	0.097	−0.06	0.31	0.31
Na ⁺					1	0.56	0.74	0.67	0.92	−0.09	0.14	0.03
K ⁺						1	0.53	0.38	0.53	−0.02	−0.21	−0.16
Mg ²⁺							1	0.58	0.81	−0.23	0.19	0.13
Ca ²⁺								1	0.86	−0.31	0.40	0.33
TDS									1	−0.23	0.29	0.2
pH										1	−0.27	−0.14
T°											1	0.78
Depth												1

Bold refers to the degrees of correlation between physico-chemical parameters. Numbers in bold correspond to the parameters with a very significant correlation.

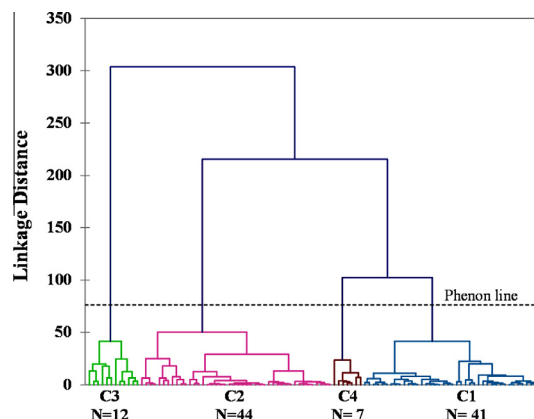


Fig. 4. HCA dendrogram determined using wards linkage method classifying groundwater from the CT aquifer into groups.

These clusters were in turn described by the principal components PC1, PC2 and PC3, respectively, resulting from the PCA (Fig. 7). According to the PCA results, 72% of the total variance of the data set is accounted for by the three first components (PC1: 43%, PC2: 21% and PC3: 8%). This percentage is relatively low, compared to some other studies (Cérón et al., 1999), probably due to the large degree of complexity of factors controlling water chemistry in such aquifers as large as the CT. Fig. 7(a–c) illustrates the position of variables (physico-chemical parameters) and of individual samples (observations) with respect to these three principal components, for each cluster generated from the HCA.

It appears that PC1 is clearly associated with TDS and major ions and corresponds to the dissolution of calcite, dolomite, gypsum and halite. Consequently, the four HCA clusters, which are well differentiated according to their mineralization, are also well distinguished with respect to the PCA components. Thus, water samples plot as relatively organized groups from C2 to C1, C4 and C3 clusters along the PC1 axis (Fig. 7a and b).

Standing out along the PC2 axis is the isolated positive value related to depth and temperature. This illustrates that the chemical composition is in general randomly distributed within the basin, with no systematic correlation with depth, except for the five samples from the Mio-Pliocene sands in the Chott Gharsa plain (#MC95, #MC96, #MC97, #MC98 and #MC99), where deepest water have been sampled. Also noticeable is the negative value for NO₃[−], which is enriched only in the few shallowest wells probably under direct influence of agricultural practices.

The third principal component (PC3) appears as dominant in pH and bicarbonate (Fig. 7b and c), which are thus weakly correlated with the other variables (Table 3). These observations corroborate in the one hand, with box plot diagrams (Fig. 6) where all clusters

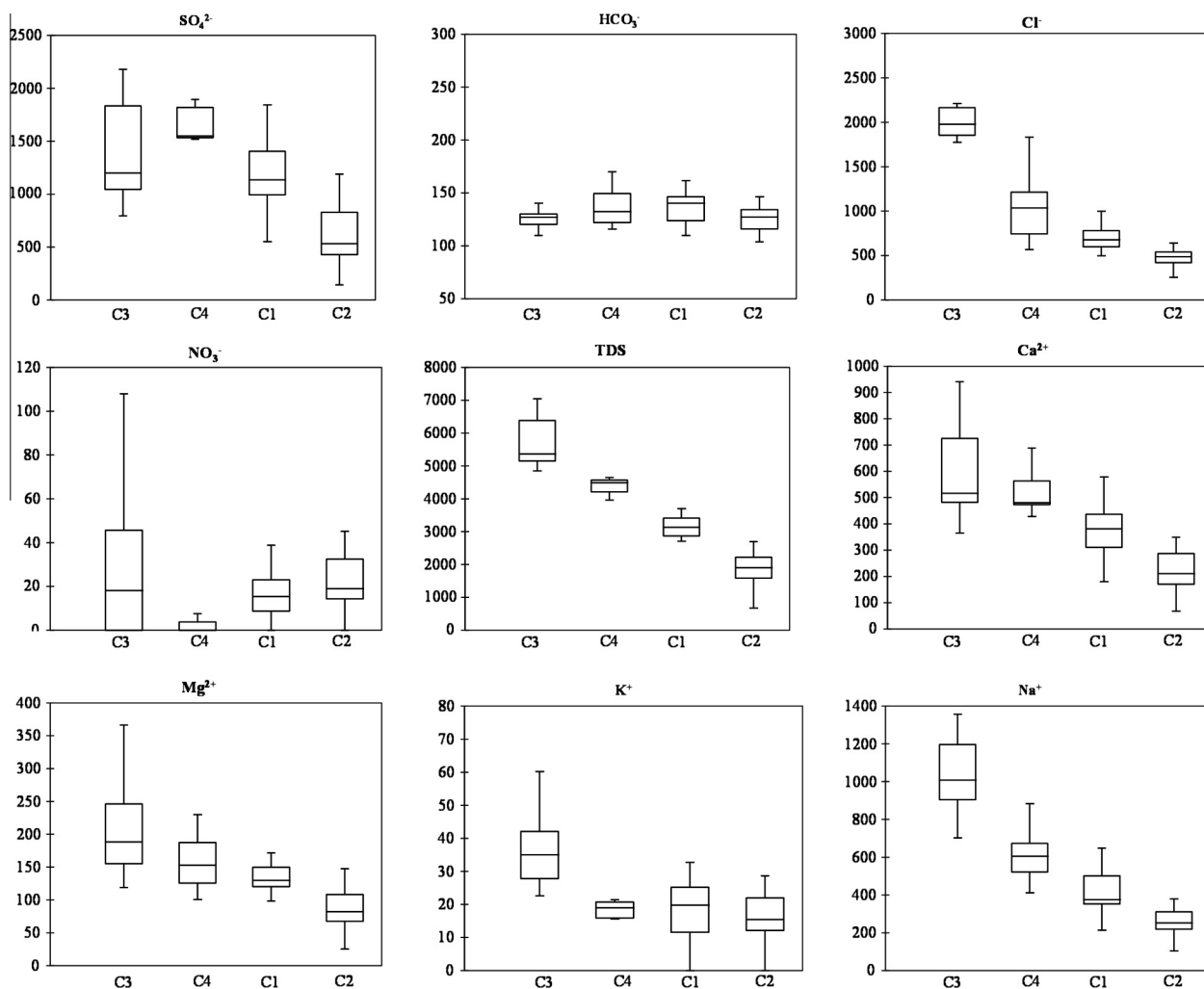


Fig. 5. Box plots of K^+ , Ca^{2+} , Mg^{2+} , Na^+ , Cl^- , SO_4^{2-} , NO_3^- , HCO_3^- and TDS for groundwater clusters 1, 2, 3 and 4.

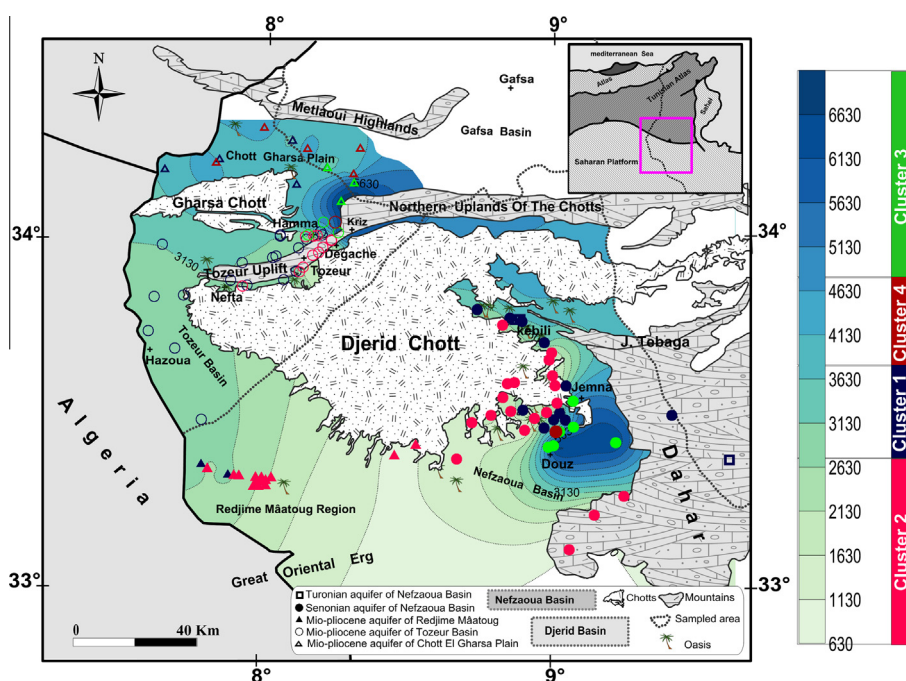


Fig. 6. Spatial distribution of TDS for groundwater clusters.

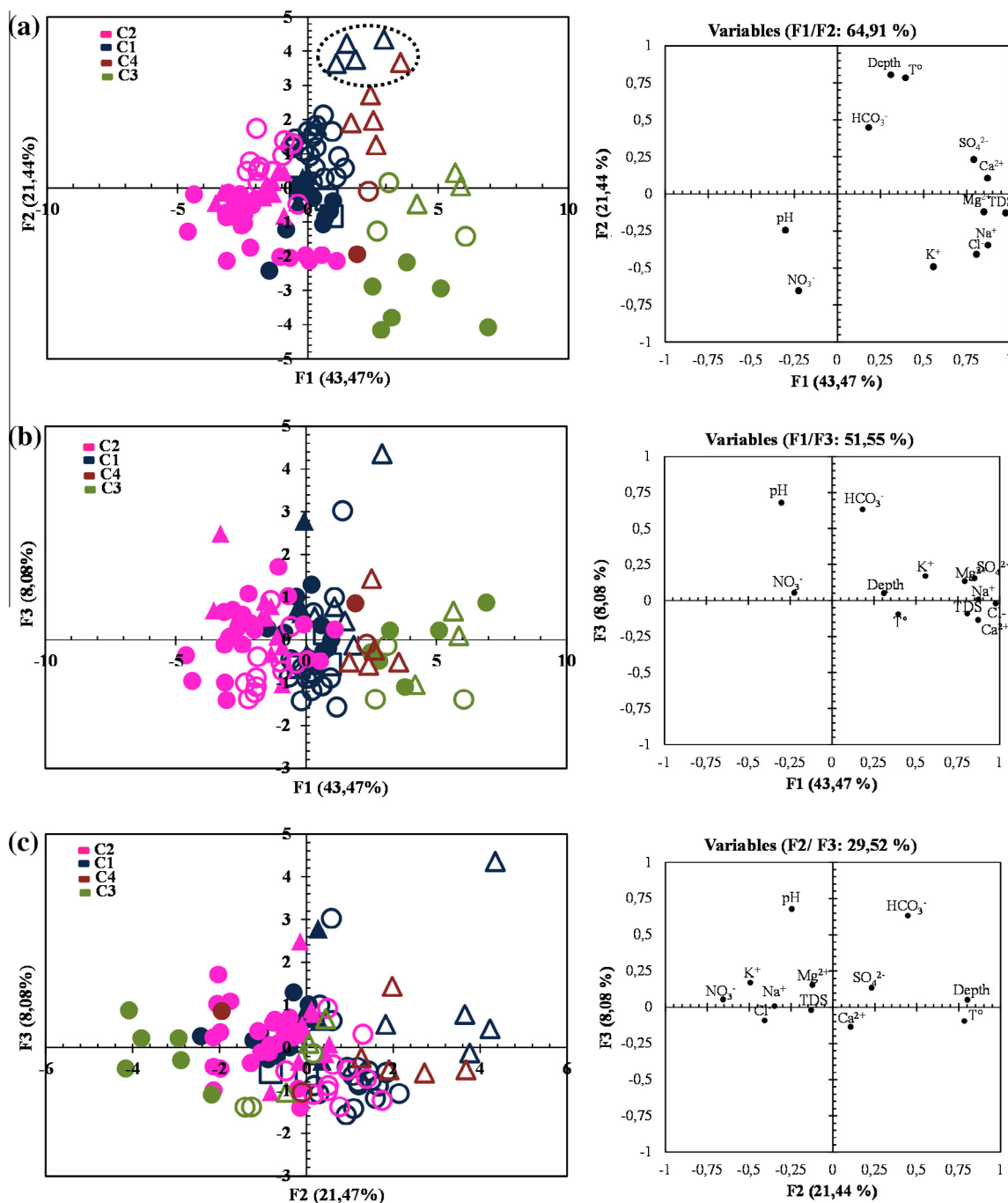


Fig. 7. Results of PCA showing the three PCs. Variables (chemical parameters) graph and individual (observations) graphs.

have the same range of HCO_3^- content and on the other hand, with the oversaturated state of all samples with respect to calcite.

The distribution of saturation indices (SI) for the major mineral phases (Fig. 8) that may regulate the concentration of major elements in groundwater reveals that all samples have an oversaturated state with respect to calcite (Fig. 8a) and that the majority of samples are also saturated with respect to dolomite (Fig. 8b), except for samples #S49, #MT82, #MT87 and #MT91. Conversely, all samples are undersaturated with respect to gypsum and halite (Fig. 8c and d). The concentration of sulfate and of sodium in these groundwaters is likely to be controlled by the dissolution of evaporitic salts (gypsum, halite) that are

present in the Cretaceous–Tertiary strata, the main formation of the major part of the basin.

Stable isotopes compositions range from -7.78‰ to -4.03‰ VSMOW for $\delta^{18}\text{O}$ and from -57.38‰ to -34.77‰ VSMOW for $\delta^2\text{H}$ (Fig. 12). Only three samples (#MT61, #MT66 and #MC103) plot on the Sfax Meteoric Water Line (SMWL) (Maliki et al., 2000) and Global Meteoric Water line. These samples located in Tozeur and Chott Gharsa areas likely indicate a modern recharge occurring in the Mio-Pliocene sands. All other samples show depleted isotopic signatures. Samples from the Mio-Pliocene aquifer of Chott El Gharsa defines alone the most depleted end-member. At the other extreme, the Mio-Pliocene samples from

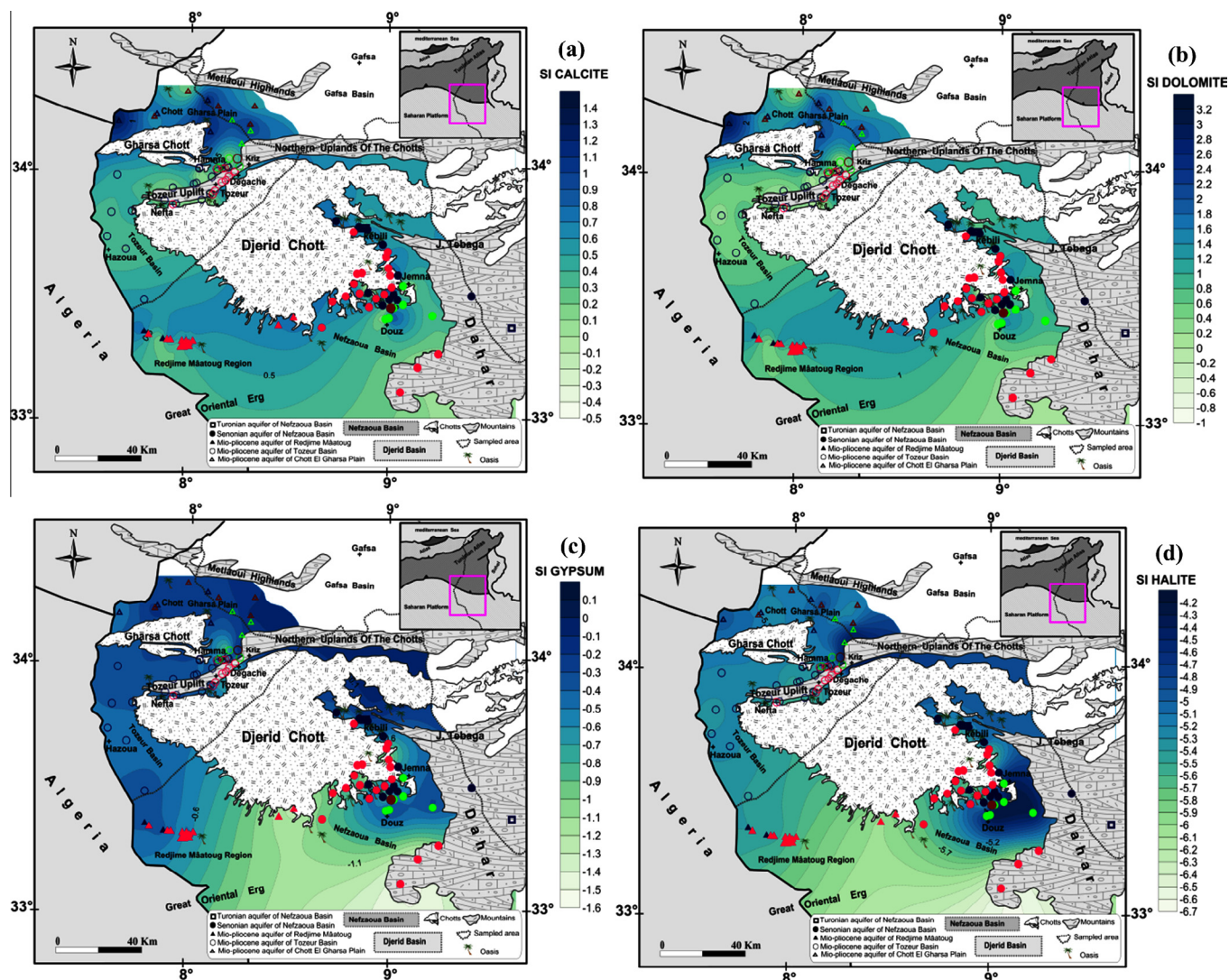


Fig. 8. Spatial distribution of saturation indices with respect to (a) calcite, (b) dolomite, (c) gypsum and (d) halite for groundwater clusters.

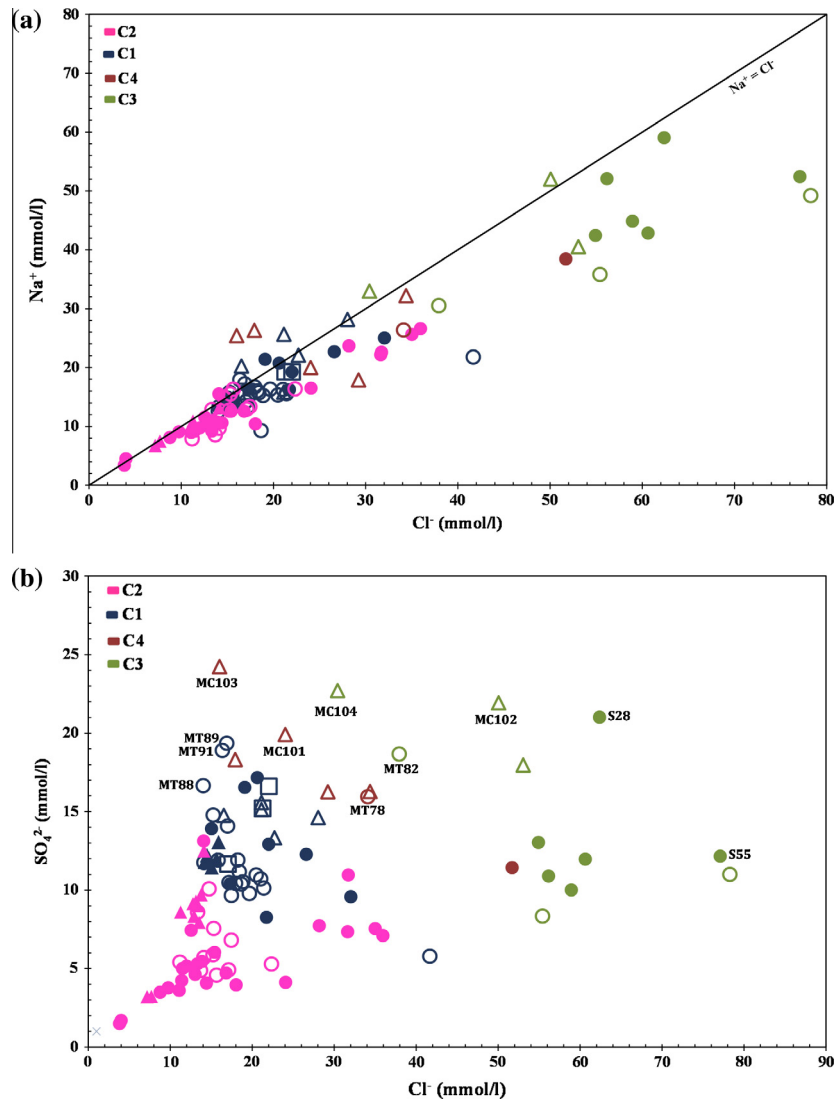
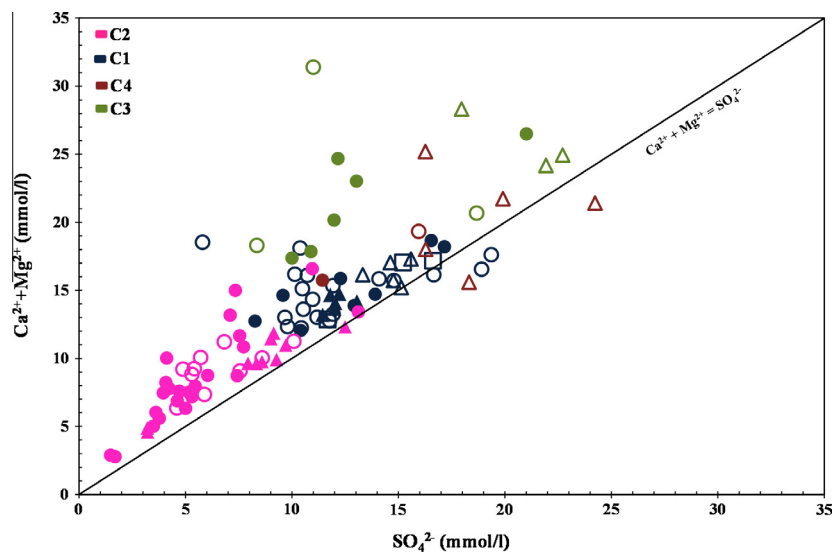
the Tozeur and Redjime Mâatoug areas overlap on the most enriched values. The Senonian samples of Nefzaoua region are in intermediate position between these groups. Samples #T1, #T2 and #T3 that tapped the Turonian layer are the most depleted samples of the Nefzaoua basin.

Most of samples are scattered along a line characterized by a slope less than 8. This reveals that significant evaporation occurred during water infiltration, especially in the Mio-pliocene sands of Redjime Mâatoug and Tozeur regions and in the Senonian carbonates of Nefzaoua basin. With the exception of the three samples that plot on Sfax Meteoric Water Line, all samples plot well below the two Meteoric Water Lines, suggesting that paleo-rainfall were characterized by lower Deuterium excess values than present-day precipitation. This likely indicates that conditions, mainly relative humidity, prevailing in the oceanic moisture source regions where these precipitations originate may have varied during the early- to mid-Holocene recharge period with respect to modern period (Merlivat and Jouzel, 1979; Pfahl and Sodemann, 2014).

5. Discussion

A first interesting observation obtained from our data is that groundwater chemistry in the CT aquifer is not primary controlled

by the main lithological characteristics of the sedimentary rocks containing the aquifer layers. Indeed, the different lithological facies, either limestone or sandy, are evenly distributed among the four clusters obtained from the HCA. This can also be illustrated in the correlation plots of major anions and cations in Figs. 9 and 10, where the different rock-types cover similar ranges of variation, and are all represented in the different end-members. This indicates that weathering of the main minerals or intergranular cements of the reservoir rocks is not the main source of major dissolved ions, which instead originate mostly from the dissolution of evaporitic formations reflected by the dominance of sulfate and chloride anions. The absence of clear-cut distinction between the chemical compositions of the waters from different aquifer levels suggest that these evaporates may be encountered indifferently within the different sedimentary layers. It is not easy to infer precise information about the exact nature and the geographical extension of these evaporates within the strata, although some significant features may be noticed in Figs. 6 and 8. For instance, it must be emphasized that groundwater from the sandy Mio-Pliocene layer from Chott El Gharsa area have in general higher TDS values than in the other regions, and that the chemistry of some of these samples is dominated by sulfate (e.g. Oued Shili 4 (#MC101), Thalja (#MC103), Oued Shili 3 (#MC104)), while others are enriched in both sulfate and chloride (e.g. Gouifla (#MC102)).

Fig. 9. Relation between (a) Na and Cl and (b) SO_4 and Cl.Fig. 10. Relation between $\text{Ca}^{2+} + \text{Mg}^{2+}$ and SO_4 .

Similarly, among the Tozeur Mio Pliocene samples, the two localities of Kriz and Dghoumes stand out with highest chloride contents and lowest SO_4/Cl ratios, while three samples are enriched in sulfate with $\text{SO}_4/\text{Cl} > 1$ (#MT88, #MT89, #MT91), and two are enriched in both (#MT78, #MT82).

The Senonian aquifer samples are also distributed evenly in the same triangular array in Fig. 9b, with two localities with high chloride (Dhmirina #S28, El Hsay #S55) and intermediate SO_4/Cl ratio. By comparison, the samples from Redjime Maatoug show a much narrower range of variation and a simple linear correlation between sulfate and chloride. The pattern of distribution of the evaporate slabs or pockets, dominated either by halite or gypsum, appears thus as patchy and widely spread over the entire basin.

Apart from the localization of these most saline waters, some information may also be obtained by comparing the regional trends of chemical composition with the direction of flow inferred from the present piezometric map. For instance, a general trend of increasing salt content is observed from SE to NW in the Redjime Maatoug basin, coherent with the regular piezometric gradient computed in this region (Fig. 3). The less saline waters (Sabria Mol #MR8 and Franing pétrolier #MR10) are found in upstream position of the inferred flow line, and the chemical composition of the samples is thus compatible with a progressive dissolution of evaporitic salt of approximately constant composition, along the flow.

By comparison, the situation is more complex among the Senonian samples of the Nefzaoua basin and Kebili region. Indeed, in this case, the less saline compositions (C2 cluster in the HCA) are mostly gathered in a deeper, inner rim under the south-eastern edge of Chott El Djerid, thus in downstream position with respect to the flow line direction descending from the Dahar range. Although the two freshest samples of the entire NWSAS are indeed found in the south-eastern of the area (#S29, #S49) as expected from the recharge zone associated with the Dahar mountain, all the samples further downstream, in the region between Douz and Jemna, belong to the C1, C3 and C4 clusters, thus saltier than those from the southern edge of the Chott El Djerid (cluster C2). Three interpretations can be proposed to explain this pattern: (i) Senonian groundwaters receive fresh recharge in an intermediate zone downstream, on the southern edge of the Chott region; (ii) the boreholes tap different disconnected levels within the Senonian strata between the two regions, the one under the Chott with a lower density of evaporate deposits, inducing lower salt content in the groundwater; and (iii) the Senonian aquifer suffers contamination from shallower aquifer or surface waters, under the Douz-Jemna region.

Anthropogenic contamination may also be suspected in this region based on higher nitrate contents than in other parts of the basin. The presence of nitrate indicates aerobic or nitrate oxidation conditions. Among the eight samples with nitrate content higher than 40 mg/l (Fig. 5), seven are from the Senonian aquifer, most of them from the Douz-Jemna area. The majority of these waters were thus sampled from boreholes with screen depth less than 50 m, an indication that nitrate may come from anthropogenic sources or from mixing with shallow aquifers influenced by agricultural practices in irrigated areas (El-Fahem et al., 2004; Marlet et al., 2007; Zammouri et al., 2009). Elevated concentrations of Na^+ and Cl^- observed in some of these samples could result from evaporation of irrigation excess water during the drought period.

The spatial distribution of chemical composition is also complex in the northwestern part of the Tunisian CT (Tozeur region and Chott El Gharsa Mio-pliocene). The samples with lowest dissolved load (C2 cluster) are restricted in a region between Kriz and Tozeur, along the Tozeur uplift, suggesting that recharge of the CT may also occur in this region, crosscut by numerous tectonic faults and characterized by shallower depth of the sedimentary strata that

culminate close to the surface in some areas. However, three samples from the C3 cluster, among the most mineralized, are also encountered in the same area, northward from Kriz, at the southern edge of Chott El Gharsa. In this case, salinization has been attributed previously to upflow leakage of saline water from a Senonian deeper level, due to the influence of over-pumping. Indeed, previous electric prospecting carried out in this area demonstrated the existence of a Senonian limestone level with very high salinity (Ricolvi, 1973), which may contaminate the overlying Mio-Pliocene sandy aquifer in Kriz and Cedada localities (El Oudiane area).

Finally, the eastern and northern edges of the Chott El Gharsa plain are bordered by C4 samples with high salt contents, which characterize the entire set of Mio-Pliocene samples from this region. In this deep-seated aquifer, located in the most downstream position along the flow lines, the simplest explanation of the high dissolved load is a large abundance of evaporitic formations, alternatively dominated by halite or gypsum.

Beyond those considerations derived from the spatial patterns, some more insight on the chemical processes regulating the groundwater composition may be obtained by looking at the major ions content, by comparison with the stoichiometry expected from the main salts dissolution. Figs. 9(a and b) and 10 confirm that the correlation between Na^+ and Cl^- , and between SO_4^{2-} and Ca^{2+} and Mg^{2+} , are compatible with a first order control of major ions by dissolution of halite and gypsum and magnesium sulfate, respectively. Furthermore, as noted in Table 3, the high positive correlation between SO_4 , Ca and Mg (0.72 and 0.74 respectively), Na and Cl (0.94) and the low correlation between Ca and HCO_3 (0.12) corroborate the interpretation of PC1 as they are consistent with evaporitic mineral dissolution. These observations could be also confirmed by the fact that most groundwaters reach calcite and dolomite saturation (Fig. 8a and b) but are undersaturated with gypsum (Fig. 8c) and halite (Fig. 8d).

However, it is also seen that a number of points deviate from this first order relationship, toward a depletion in sodium, corresponding with an enrichment in alkaline earth elements. This is further illustrated in Fig. 11, where the sum $([\text{Ca}^{2+}] + [\text{Mg}^{2+}] - [\text{HCO}_3^-] - [\text{SO}_4^{2-}])$ is plotted against $([\text{Na}^+] + [\text{K}^+] - [\text{Cl}^-])$ (in meq/l), showing that the deficit in dissolved sodium with respect to pure halite dissolution, is indeed compensated quantitatively by the excess in calcium and magnesium with respect to pure gypsum dissolution. We can see in Fig. 11 that a large majority of samples lie on the negative values along the 1:1 line representing neutral charge balance. The deficit in sodium may reach 25 mmol/l in the most depleted sample, for a chloride concentration of 80 mmol/l. It is commonly on the order of 30%, and is observed in samples from either one of the limestone or Mio-Pliocene layers, as well as for different dissolved loads.

These features have been related by several authors to cation exchange on mineral surfaces, upon which calcium and magnesium are desorbed from solid phases into the dissolved phase, due to replacement by sodium (Hiscock, 2005; Chae et al., 2006). However, although potentially compatible with the observations, this hypothesis still faces unanswered questions. Cation exchange has been demonstrated and described in detail in cases where aquifers were submitted to large changes in chemical conditions, typical for instance of saline intrusion in coastal aquifers, or on the contrary, of freshening of a previously brackish aquifer (Appelo and Postma, 1996). The exact process that could generate a similar chemical front, able to displace surface adsorption equilibria, has still to be specified in the case of relatively diluted solutions in deep seated aquifers. The source of excess calcium has also to be identified, and the model requires a quite complex multistage evolution, involving first saturation of surface sites by calcium and magnesium, then change of conditions toward sodium saturation.

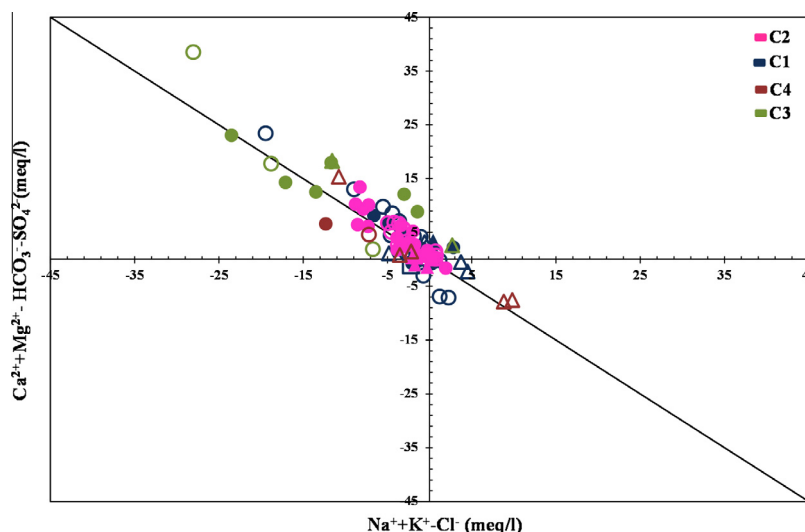


Fig. 11. Diagram indicating cation exchange process.

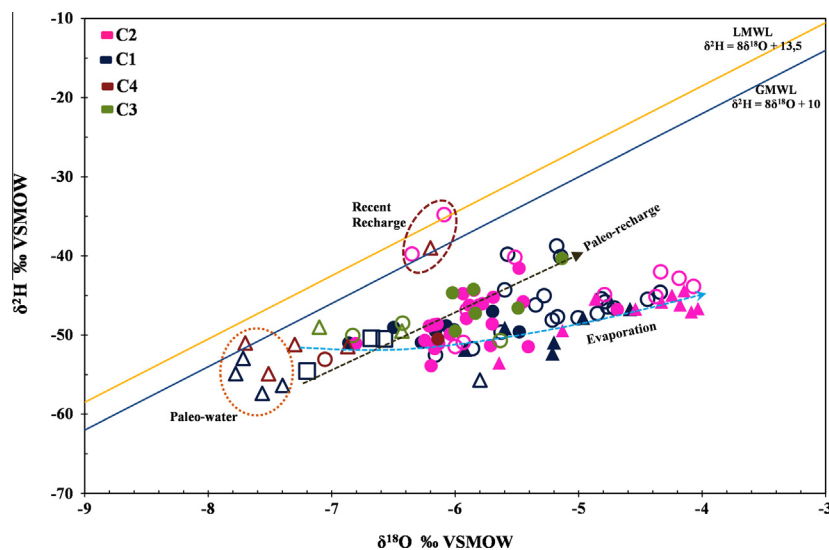


Fig. 12. Relation between $\delta^{18}\text{O}$ and $\delta^2\text{H}$ (‰ VSMOW) in the CT groundwaters. Also shown for reference are the Sfax Meteoric Water Line (SMWL) ($\delta^2\text{H} = 8\delta^{18}\text{O} + 13.5$, Maliki et al., 2000) and the Global Meteoric Water Line (GMWL), ($\delta^2\text{H} = 8\delta^{18}\text{O} + 10$, Craig, 1961).

If these surface exchange processes may have occurred to some extent, we cannot rule out that other processes, such as dissolution of calcium chloride, could account for the observations. This raises the question of CaCl_2 origin in these formations. Garrett (2004) proposes that calcium chloride could be formed by the partial-to-complete dolomitization reaction with calcite in presence of magnesium chloride. However, this hypothesis should be checked and the exact nature and origin of the calcium chloride in the studied aquifers have to be identified.

Regarding their isotopic signatures, the CT groundwaters are depleted with respect to modern precipitation with the exception of some boreholes from the Tozeur and Chott Gharsa Mio-Pliocene sands that lie on the local meteoric water line. This is in agreement with the general depletion observed in the isotopic composition of aquifers across Sahara (Edmunds et al., 2004).

If this clearly indicates that most of the recharge of the CT system occurred during different climatic conditions compared to the present day, it has been frequently assume that this overall isotopic depletion represents colder conditions during past more pluvial periods. Consequently, it has been concluded that these

paleogroundwaters might have derived from glacial recharge (see for example Abouelmagda et al., 2012). However, recent climate simulations contradict this common contention. Using a fully coupled atmosphere–ocean general circulation model (GCM) that explicitly tracks water isotopes, LeGrande and Schmidt (2009) simulate that during the early- to mid-Holocene (at 9 ka and 6 ka), that is to say during the Holocene Climatic Optimum, $\delta^{18}\text{O}$ of precipitation are depleted by several percent compared with modern rainfall over the Northern Africa. This general trend in isotopic composition is accompanied by a general increase of precipitation and a small drop of temperature (LeGrande and Schmidt, 2009). This is in agreement with recharge temperature derived from Noble Gas data (NGT) that roughly indicate slightly cooler recharge temperature (averaging 19.7 °C, to be compared to the present day mean annual temperature of 21 °C) for CT groundwater from Algeria (Guendouz et al., 1997). Considering stable isotope data together with Noble Gas Temperatures and with ^{14}C data that constrain CT groundwater ages to be younger than 15 ka (Abid et al., 2011), we infer that the recharge of CT groundwater started during the deglacial period and occurred during the Holocene Climatic

Optimum. This is in general agreement with the model proposed by LeGrande and Schmidt (2009) that captures the mean features of the regional variability of proxy climate tracers, especially the changes in stable isotopic composition of rainfall during the early- to mid-Holocene in Saharan regions (Guo et al., 2000). As previously suggested by these authors, stable isotopes do reflect regional hydrological cycle changes rather than as indicators of changes in local temperature.

6. Conclusion

The CT aquifer in southern Tunisia has been investigated by both statistical and geochemical methods in order to identify regional factors and processes controlling groundwater chemistry. Dataset interpretation highlighted that the chemical composition of these groundwaters is extremely spatially variable with no predominant control of the lithological facies on the water chemistry.

The four water groups obtained by the multivariate statistical analyses could be globally discussed as two water types. The first one is characterized by low to intermediate salinity ($600 < \text{TDS} < 3700 \text{ mg/l}$) and involve groundwater mainly located in the major part of the basin. Water compositions reveal that the mineralization is mainly regulated by water/rock interaction through mineral dissolution and probably by ions exchange processes enhanced by long groundwater residence time. The second water type has high salinity ($3700 < \text{TDS} < 7000$) observed in some points with specific local effects such as irrigation return flow or mixing with shallow and/or deep aquifers. Indeed, the hydrogeochemical data and interpretations show that below 50 m, most groundwater samples are saline and are therefore indicative of mixing with more saline waters as shown in Douz, El Hsay, Kriz and El Oudiane localities.

Geochemical investigations carried out on the CT aquifer have highlighted that the mineralization, even extremely variable, is controlled by the water/rock interactions enhanced by the long residence time of groundwater. However, local possible sources of salts are likely related to human activities such as agriculture practices what should be considered in the aquifer vulnerability assessment in order to better protect and manage these water resources.

Most groundwaters have a $^2\text{H}/^{18}\text{O}$ fingerprint that plotted below the global meteoric water line in a domain indicating paleo-recharge and/or enhanced evaporation effect. This significant depletion is consistent with simulated isotopic composition of rainfall obtained from a water-isotope enabled, coupled atmosphere–ocean general circulation model that derived overall $\delta^{18}\text{O}$ depletion in rainfall during the early- to mid-Holocene period in the Saharan regions. Consistently with available NGT data and ^{14}C ages, we infer that most of the paleorecharge of the Tunisian part of the CT aquifer occurred during the early- to mid-Holocene.

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