

Spontaneous Article

Integrated statistical and hydro-geochemical approach to identify the origin and process of saline contamination of Remila plain groundwater (Khenchela, Algeria)

Laiche AOUIDANE^{1*} , Mohamed BELHAMRA² and Asma KHEDDOUMA³

¹ Agricultural Sciences Department, Faculty of Nature and Life Sciences, University of Abbes Laghrour Khenchela, BP 1252 Route de Batna, Khenchela 40004, Algeria.

² Department of Agricultural Sciences, University of Mohamed Khider, BP 145 RP, Biskra 07000, Algeria.

³ Department of Biology, Faculty of Nature and Life Sciences, University of Abbes Laghrour Khenchela, BP 1252 Route de Batna, Khenchela 40004, Algeria.

*Corresponding author. Email: laiche_a@yahoo.fr

ABSTRACT: Groundwater is widely used in the semi-arid region of Remila plain (Khenchela, Algeria) for urban and agricultural supplies. An integrated statistical and hydro-geochemical approach was performed with 70 water samples in order to identify the main processes and the origin of water salinisation. The results have suggested the dominance of three chemical facies: Sulphato chloruro calcic ($\text{SO}_4\text{-Cl-Ca}$) in the northeastern part, Sulphato chloruro calci magnisian ($\text{SO}_4\text{-Cl-Ca-Mg}$) in most of the waters and alkali-earth bicarbonate ($\text{HCO}_3\text{-Ca-Mg}$) in the southeastern part. Although based on principal component analysis and hierarchical clustering analysis, the statistical approach identified three water groups: (1) saline water (17%; total dissolved solids $>1000 \text{ mg l}^{-1}$ with the dominance of Sulphate (SO_4^{2-})); (2) moderately saline water (17%) with a dominance of bicarbonate (HCO_3^-); and (3) moderately saline water (66%) with mixed facies. The binary diagrams confirmed the predominance of three processes: evaporite dissolution and/or precipitation, combined by ionic exchange. In the northeastern part of the area, however, another process was detected – the saline intrusion of Sabkha water, favoured by extensive groundwater use.

KEY WORDS: hydro-geochemistry, salinity, semi-arid, statistics.

Freshwater resources represent only 3% of the world's water and are mainly in frozen form, in which groundwater represent for only 30% (Cassardo & Jones 2011). Although groundwater has become an important source of freshwater for the domestic, industrial and agricultural sectors around the world, especially in arid and semi-arid regions, it has become a primary source of freshwater supply (Bouzourra *et al.* 2015; Aouidane 2017). In the southern Mediterranean regions, groundwater is the predominant source of agricultural and industrial use (Siebert *et al.* 2010). In Algeria, 67% of irrigated land is irrigated by groundwater (Zektser & Loaiciga 1993). Indeed, groundwater quality plays a crucial role in plant growth, human health and environmental. Yet, some natural processes can degrade these qualities, and these processes are increasing by human activities due to resource overexploitation. (Rina *et al.* 2013; Masoud *et al.* 2018). Therefore, it is important for the sustainable management of these resources to identify the geochemical processes that control groundwater.

The salinisation is one of the most prevalent pollution problems of water resources, especially in arid and semi-arid regions. Indeed, salinisation of groundwater is a global concern not only for the sustainable exploration of water resources but also for the protection of natural ecosystems (Pisinaras *et al.* 2010; Li *et al.* 2016). Over the last few decades, salinisation of groundwater

has become the subject of considerable research (Gibbs 1970; Hsissoua *et al.* 1996; Yermani *et al.* 2003; Pazand & Hezarkhani 2012; Grillot & Schoeller 2015; Aouidane & Belhamra 2017). This problem can be attributed to natural and/or anthropogenic factors, such as the interaction of water rocks (Frape *et al.* 1984; García & Blesa 2001; Ghesquière *et al.* 2015), the saline intrusion of saline coastal water or Sabkha saline water (Capaccioni *et al.* 2005; Wang & Jiao 2012) and fossil sea water (Tijani 2004; Akouvi *et al.* 2008; Farid *et al.* 2013). Furthermore, anthropogenic intervention has accelerated natural degradation processes through saline water intrusion due to overexploitation of groundwater, inadequate sewage disposal and residues from intensive agricultural and industrial activities (Bouderbala 2015; Zewdu *et al.* 2017).

Many approaches can be used to identify the geochemical processes of groundwater, including the use of binary ratios of minor and major tracers (Scanlon *et al.* 2006; Gil-márquez *et al.* 2017), isotopic tracers (Ghabayen *et al.* 2006; Hassen *et al.* 2016) and statistical analysis (Kharroubi *et al.* 2012; Viswanath *et al.* 2015; Masoud *et al.* 2018).

Within this context, our study focuses on a semi-arid region – that of the Remila endorheic basin in northeastern Algeria, characterised by low rainfall, with a temporal and sporadic distribution. The region is considered an agricultural area with a



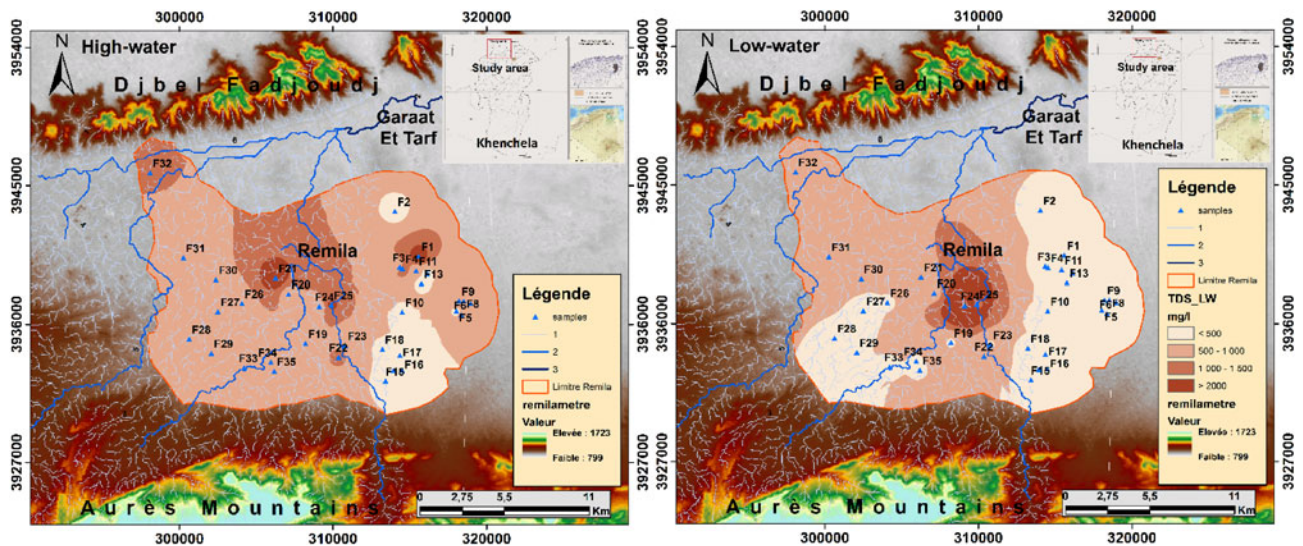


Figure 1 Map showing location and spatial salinity distribution (TD) (high-water and low-water) of groundwater Remila (Khenchela).

population of more than 47,000 people, of which 800 ha are irrigated. However, the water supply comes mainly from groundwater through more than 500 boreholes. Therefore, as part of improving the quality management of the water supplies in this region, it is important to understand the main processes that control the mineralisation of this water.

The main aim of this study is to identify factors that control groundwater salinity. An integrated hydrogeological, hydrochemical and statistical approach was used: (1) for the assessment of groundwater chemistry to highlight dominant groundwater mineralisation processes; (2) to use statistical analyses to identify distinct water groups and to assess the correlation between different elements and factors of water hydrochemistry; and (3) to identify recharge areas and major sources of contamination. A better understanding of the sources of salinisation and contamination of Remila aquifer system (Khenchela) will then serve as an important scientific basis for the study areas of water resource planning and management.

1. Materials and methods

1.1. Study area

The study area forms part of the Garaat Et Tarf endorheic basin in northeastern Algeria. It lies approximately on latitudes [35° 25'N–35°40'N] and longitudes [06°30'E–07°05'E], with a uniform topography covering an area of 250 km² where the altitude is between 800 and 1000 m. Geographically, the study area is bounded by Djebel Fdjoudj massif in the N, the saline depressions of Sabkha Garaat Et Tarf in the E and the northern slopes of Aurès Mountains in the S and W (Fig. 1) (C.P.H. 1977). The semi-arid climate of the region is characterised by annual rainfall of less than 400 mm with an average annual temperature of 17 °C, with minimum temperatures in January (6 °C) and maximum temperatures in August (30 °C), while the annual potential evapotranspiration is 1050 mm (K.M.S. 2014). Indeed, in the study area the surface water is scarce and periodic, so the water supply depends heavily on groundwater to meet the needs of a rural population of 47,000 inhabitants and in addition to the irrigation of an area of 800 ha.

1.1.1. Geological setting. The study region is characterised from a geological point of view by endorheic basins, where runoff converges into the inner lowlands and forms the Sabkha (salt depression) with a length of 50–60 km and a mean width of 20 km. As a whole, it represents a Mio–Pliocene floodplain with Quaternary deposits transported by streams and then deposited

in a sequence of floodplains due to the flow regimes of the streams (Laffitte 1939; C.G.G. 1969). Middle Cretaceous (Aptian) or Upper Cretaceous (Cenomanian, Turonian and Senonian) formations are the cretaceous formations surrounding the study area, covering the northern and southern part of the region. While in the NW parts, the Miocene is presented by a deposit of limestone–sandstone and limestone (Burdigalian), which are discordantly arranged on the Cretaceous and Pontian red marl. The eastern parts of the plain are surrounded by an endorheic salt depression (Sabkha Great ET Tart) (Vila 1977). Thus, the lithostratigraphy of Remila plain is described by recent Quaternary soils.

1.1.2. Hydrogeological setting. In the study area, the hydrographic system distribution is related to the evolution of the structural phenomena. The hydrographic network is typified by a significant intensity with a temporary flow during the wet seasons. The most important stream is Boulefreis, which drains the whole region from NE to SW, but also there is the stream of Baghai that drains the eastern part, meeting Maarouf and Gueiss streams in the centre. All these streams flow into a closed low surface (Sabkha of Garaat Etarf) (D.H.W.K. 1984).

Remila aquifer exists in a sandy–marly limestone substratum of the Moi–Plio–Quaternary. Aquifer recharge is maintained through the drainage of runoff water from the northern slope of Aures. The MPQ aquifer is represented by two water tables, located in the alluvial filling of the plain (C.G.G. 1969).

1.2. Sample collection

During two campaigns, 70 groundwater samples were taken to identify the dominant hydro-geochemical processes in Remila aquifer system. The first campaign was collected in the low-water period in December–October 2013, after a dry season, whereas the second was collected in the high-water period from May to June 2014, after a wet season. We used methods recommended by Rodier *et al.* (2009) in the sampling and analysis to minimise handling errors. Sampling and measurements were carried out on functional boreholes. In fact, the borehole water was pumped two or three times before sampling, with regular monitoring of the electrical conductivity (EC) at the same time until the values were stable.

The samples from the water were untreated and raw. Water was collected from a pre-rinsed 1-L polyethylene bottle and filtered through a membrane filter of 0.45 µm. The bottles were filled to minimise exposure to air, and transported in coolers (4 °C). The coordinates of the sampling have been determined using a

Table 1 Methods used for major ion and isotope analysis in the waters of Remila.

Elements	Methods of analysis
Ca ²⁺ and Na ⁺	Industrial flame photometers PFP7
Mg ²⁺ , K ⁺ , Sr ²⁺ , Al ²⁺ and Li ⁺	Perkin Elmer atomic absorption AA 200 (FXAA)
SO ₄ ²⁻ and NO ₃ ⁻	Colorimetric method
Cl ⁻ and HCO ₃ ⁻	Volumetric method

global geographic positioning system (GPS GARMIN Olathe KS, US) (Fig. 1).

1.3. Sample analysis

Water physicochemical parameters such as EC, total dissolved solids (TDS), pH and temperature were measured *in situ* using a Consort C535 multi-parameter. Also, the dosage of the other parameters was conducted at Constantine University, Algeria, in the hydro-chemical laboratory (Table 1).

All the statistical analysis of the data was carried out using STATISTICA 7.1 (StatSoft1) software. Principal component analysis (PCA), correlation table and hierarchical clustering analysis (HCA) were applied in our case.

2. Results and discussion

2.1. General hydro-chemical features

2.1.1 Distribution of groundwater salinity. The results of the groundwater physicochemical analysis are given in Table 2. Our water salinity values (TDS) during dry season ranged from 568 to 1586 mg l⁻¹, with an average of 906.3 mg l⁻¹, which indicates low to moderate mineralisation of water, whereas the TDS values in the wet season ranged from 1250 to 3270 mg l⁻¹, with an average of 1822.16 mg l⁻¹, indicating that our water had raised from moderate to high mineralisation. However, after the wet season, we observed a significant increase in saline load; this suggests that rainwater that feeds groundwater significantly affects our water's mineralisation. The pH values of the majority of the points were close to neutrality; they were between 6.5 and 7, with an average of 6.9 during the wet period, yet the values oscillate between 6.5 and 7.21, with an average of 6.91 during the dry period – this indicates a slight seasonal variation.

The results of 35 points have led to generating a spatial distribution map of salinity (TDS) (Fig. 1). Water mineralisation variations are observed from upstream to downstream (S to N). This spatial variation can be divided into two types of water: low salinity water of the southern and western parts of the plain, and moderately salty water of the northern part near the Sabkha. This can be explained by Sabkha's significant saltwater effect.

2.1.2. Hydro-chemical facies. Identifying the hydro-chemical types of water is a useful tool for assessing water chemistry and processes such as mixing, cation exchange and dissolution. The Piper diagram is considered to be the common method for performing multiple analyses on the same graph and grouping the various water into well-defined facies (Piper 1944). The results of the geochemical analysis of 70 samples are projected on the Piper diagram using DIAGRAMS 5.1 (Fig. 2). According to the results of the two companions, we can note the dominance of three water chemical facies: SO₄-Cl-Ca salt water in the northeastern part of the region near Sabkha, SO₄-Cl-Ca-Mg moderately salty water, which represents most of the points, and finally the good quality type HCO₃-Ca-Mg by meeting them in the southeastern part of the zone.

In the anionic triangle, especially after the wet period, most of the water points have shown a tendency to SO₄²⁻ dominance, while there was a tendency to Ca²⁺ dominance in the cationic triangle. This indicates that different processes affect the aquifer system: dissolution and/or precipitation, ion exchange and salt-water intrusion of Sabkha water.

2.2. Statistical analysis

Descriptive statistical evaluation of data is a critical step in any statistical analysis (Table 2) (Yang *et al.* 2011; Hosseini *et al.* 2014). The most important factor that can describe the variability of the water parameter values is the variance coefficient (VC). A low VC (<10%) for pH was calculated indicating a low spatial variability in the study area. While for the TDS, HCO₃⁻, Ca²⁺ and ferrous (Fe²⁺), a moderate coefficient of variance (20–50%) was observed, indicating a moderate spatial variability for these parameters, and was mainly influenced by natural factors. However, very high VC values above 50% were observed for magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), sulphate (SO₄²⁻), Chlorine (Cl⁻) and nitrate (NO₃⁻), indicating a very high spatial variability that the parameters have been affected by natural and anthropogenic factors.

Table 2 Descriptive statistics of Remila water parameters (mg l⁻¹). Abbreviations: Std. Dev = standard deviation; Coef. Var = coefficient of variation.

	Campaign	Mean	Median	Minimum	Maximum	Std. Dev.	Coef. Var.	Skewness	Kurtosis
pH	2013	6.87	6.92	6.52	7.02	0.13	1.90	-1.51	1.33
	2014	6.91	6.92	6.50	7.21	0.11	1.55	-1.27	7.09
TDS	2013	896.29	824.50	568.00	1586.00	254.52	28.40	1.29	1.13
	2014	1797.14	1710.00	1250.00	3270.00	485.57	27.02	1.67	2.87
Ca ²⁺	2013	134.74	132.26	40.08	252.50	39.36	29.21	0.49	2.41
	2014	132.14	128.26	44.09	248.50	46.42	35.13	0.76	1.18
Mg ²⁺	2013	50.83	35.88	6.96	239.64	53.54	105.34	2.63	6.50
	2014	56.83	52.68	28.80	129.48	22.48	39.55	2.04	4.59
Na ⁺	2013	55.56	41.75	11.96	145.59	34.78	62.61	1.45	1.49
	2014	69.46	62.11	29.67	162.15	33.45	48.16	0.93	0.41
K ⁺	2013	1.09	0.17	0.02	9.98	2.09	191.45	2.94	9.57
	2014	1.16	1.00	0.09	3.95	0.80	69.13	1.87	4.43
HCO ₃ ⁻	2013	174.75	164.70	54.90	280.60	53.64	30.70	0.31	-0.30
	2014	253.20	256.20	183.00	402.60	48.86	19.30	0.96	1.39
Cl ⁻	2013	122.80	118.93	35.50	312.40	58.36	47.53	1.16	2.07
	2014	125.79	117.15	35.50	333.70	83.41	66.31	1.22	0.90
SO ₄ ²⁻	2013	344.24	320.00	160.00	704.00	129.92	37.74	1.64	2.84
	2014	293.86	270.00	140.00	1250.00	188.44	64.13	4.05	20.20
NO ₃ ⁻	2013	-	-	-	-	-	-	-	-
	2014	8.19	3.60	0.20	39.00	11.09	135.45	1.96	2.42

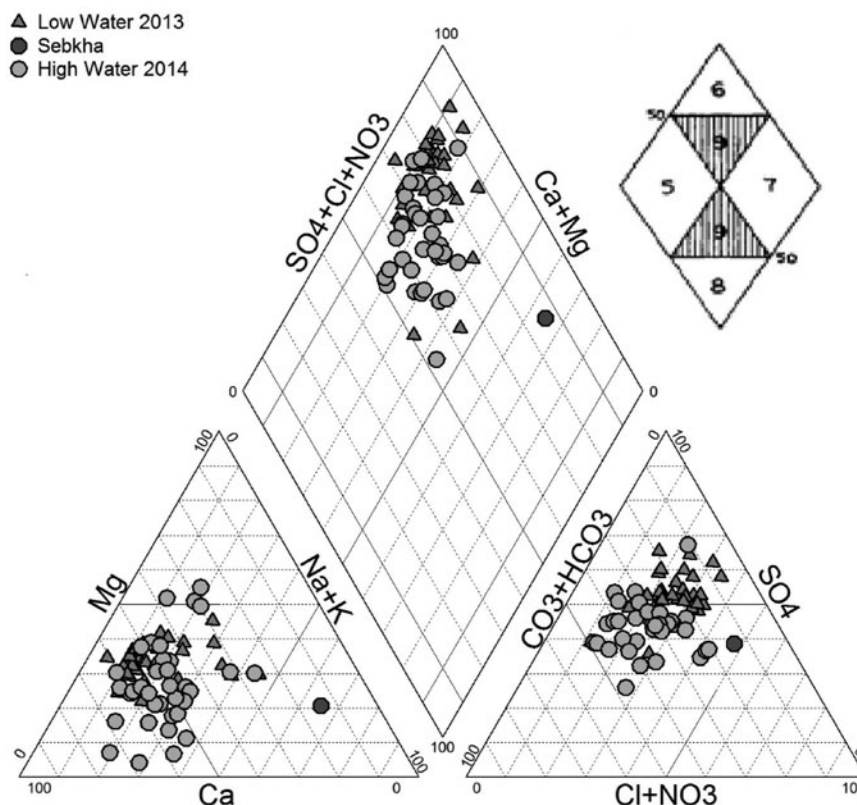


Figure 2 Piper diagram of groundwater (low-water and high-water) of the Remila.

Skewness reflects the symmetrical distribution of the data; if the values are lower than zero, all the data are below the mean, but if the values are equal to zero then the data have a normal distribution (Brovelli *et al.* 2011). The calculated skewness values of Ca^{2+} , Na^+ and HCO_3^- were close to zero, indicating that the data follow a normal distribution. However, other parameters had values >1 , and did not require a data transformation. In statistics, several researcher's studies (Kerry & Oliver 2007; Oliver 2010; Oliver & Webster 2014) have shown that if the skewness values are beyond the standard ± 1 limit, they do not necessarily mean a data transformation for a more precise analysis, especially when the data value is high.

2.2.1. Pearson's correlation matrix. Using the correlation matrix of various parameters, numerous significant correlations were established (Table 3). A strong correlation ($r > 0.7$) was found between the chemical tracers SO_4^{2-} , Cl^- , Mg^{2+} , Na^+ , Ca^{2+} , strontium (Sr^{2+}) and TDS, indicating an evaporite origin

(from halite (NaCl), anhydrite (CaSO_4), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$), epsomite (MgSO_4) or celestite (SrSO_4)) of these elements in the water. However, this was not the case for HCO_3^- , which has a low correlation with the salinity indicator TDS, explained by its low concentration in the water solution that ranges between 54.9 and 280.6 mg l^{-1} . In addition, the correlation coefficients between chloride ($r = 0.81$) and sodium ($r = 0.81$), with the (TDS), showed the same origin for these two elements. On the other side, there was a slight difference between sulphate ($r = 0.95$), magnesium ($r = 0.87$) and calcium ($r = 0.66$) correlation coefficients with TDS. This can be explained by the non-conservative transport of calcium and magnesium ions (thus, the participation of these cations in cation exchange with clay minerals that are most abundant in the area and/or in precipitation/dissolution reactions) (Van Breukelen *et al.* 1998).

Observing the relationship between anions and cations, significant correlations were found between Cl^- and Na^+ ($r = 0.55$),

Table 3 Correlation matrix of different water parameters in the Remila plain (Khenchela) (mg l^{-1}).

Variable	pH	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	Fe	Mn	Sr	Li	Al
pH	1.00													
TDS	0.16	1.00												
Ca	0.22	0.66	1.00											
Mg	0.26	0.87	0.43	1.00										
Na	0.00	0.81	0.17	0.69	1.00									
K	0.16	0.82	0.38	0.79	0.75	1.00								
HCO_3	-0.33	0.20	-0.14	-0.02	0.44	0.14	1.00							
Cl	0.31	0.81	0.74	0.68	0.55	0.65	-0.18	1.00						
SO_4	0.19	0.96	0.61	0.93	0.74	0.80	0.02	0.73	1.00					
Fe	-0.08	0.21	0.28	0.15	0.00	0.20	0.08	0.16	0.20	1.00				
Mn	0.01	-0.24	-0.36	-0.21	-0.05	-0.12	0.24	-0.44	-0.22	-0.07	1.00			
Sr	-0.01	0.71	0.58	0.57	0.45	0.62	0.34	0.46	0.66	0.36	-0.04	1.00		
Li	0.23	-0.07	-0.07	0.05	-0.07	-0.06	-0.22	-0.01	-0.02	0.12	-0.12	-0.22	1.00	
Al	0.10	-0.03	0.03	-0.03	-0.13	-0.01	-0.20	-0.03	0.03	-0.08	-0.19	-0.15	-0.04	1.00

Cl^- and Ca^{2+} ($r=0.74$), Cl^- and Mg^{2+} ($r=0.68$), Cl^- and K^+ ($r=0.65$), SO_4^{2-} and Mg^{2+} ($r=0.93$), SO_4^{2-} and Ca^{2+} ($r=0.61$). This tends to prove that most chloride came from the dissolution of sylvite (KCl) and NaCl, but a very small proportion of this anion could come from the dissolution of other minerals. The low correlation between chloride and sodium indicates the involvement of sodium ions in cation exchange with the clay substratum of the aquifer. Additionally, there was a relatively significant correlation between Cl^- with Ca^{2+} (0.74) and Mg^{2+} (0.68). This was due to the water salinity caused by many processes that characterise highly mineralised water, including cation exchange, gypsum and halite dissolutions, and this lead to the increase of calcium, magnesium and chloride concentrations, respectively.

We carried out a main PCA and HCA using the software STATISTICA 8 (Statsoft 2010) in an attempt to clarify the relationship between the chemical elements (variables) and grouping water points (individuals) with the same chemistry.

2.2.2. PCA. In order to characterise geochemistry and water types, more and more research relies on statistical analyses; the PCA approach is one of the most suggested approaches (Ayadi *et al.* 2018). In the Remila aquifer samples, the variable factors F1–F2 (Fig. 3a) show that this plane expresses 53.95 % of the expressed variance. The factor F1 (36.74 %) is negatively

determined by the majority of the elements: TDS, SO_4^{2-} , Cl^- , Mg^{2+} , K^+ , Na^+ and Ca^{2+} ; therefore, it has a mineralisation axis of evaporates and salinity. The F2 explains 17.21 % of the total variance, which is positively determined by the pH and HCO_3^- , indicating that the dissolution of carbonates does not contribute to the salinisation of waters.

The projection results, variables and individuals in the factorial plan (F1, F2), shown in Figure 3a, allow us to note three different water groups. The first type I saline water represents 17 %, has a TDS that exceeds 1000 mg l^{-1} and is characterised by a high concentration of SO_4^{2-} ; type II is moderately saline water with high concentrations of HCO_3^- and represents 17 %; and type III is moderately saline water with mixed facies, representing the majority of waters with 66 %.

2.2.3. HCA. Ascending hierarchical clustering (AHC) is a powerful multivariate statistical method used to analyse water chemistry data for geochemical model formulation (Yidana *et al.* 2008; Ahoussi *et al.* 2010).

The results from the analysis of the hierarchical ascending data classification can be observed in the dendrogram (Fig. 3b), in which three principal groupings of the variables are highlighted. The first group includes the variables: TDS, SO_4^{2-} , Mg^{2+} , K^+ , Na^+ , Cl^- , Ca^{2+} and Sr^{2+} . This grouping represents the elements that play a major role in the mineralisation of

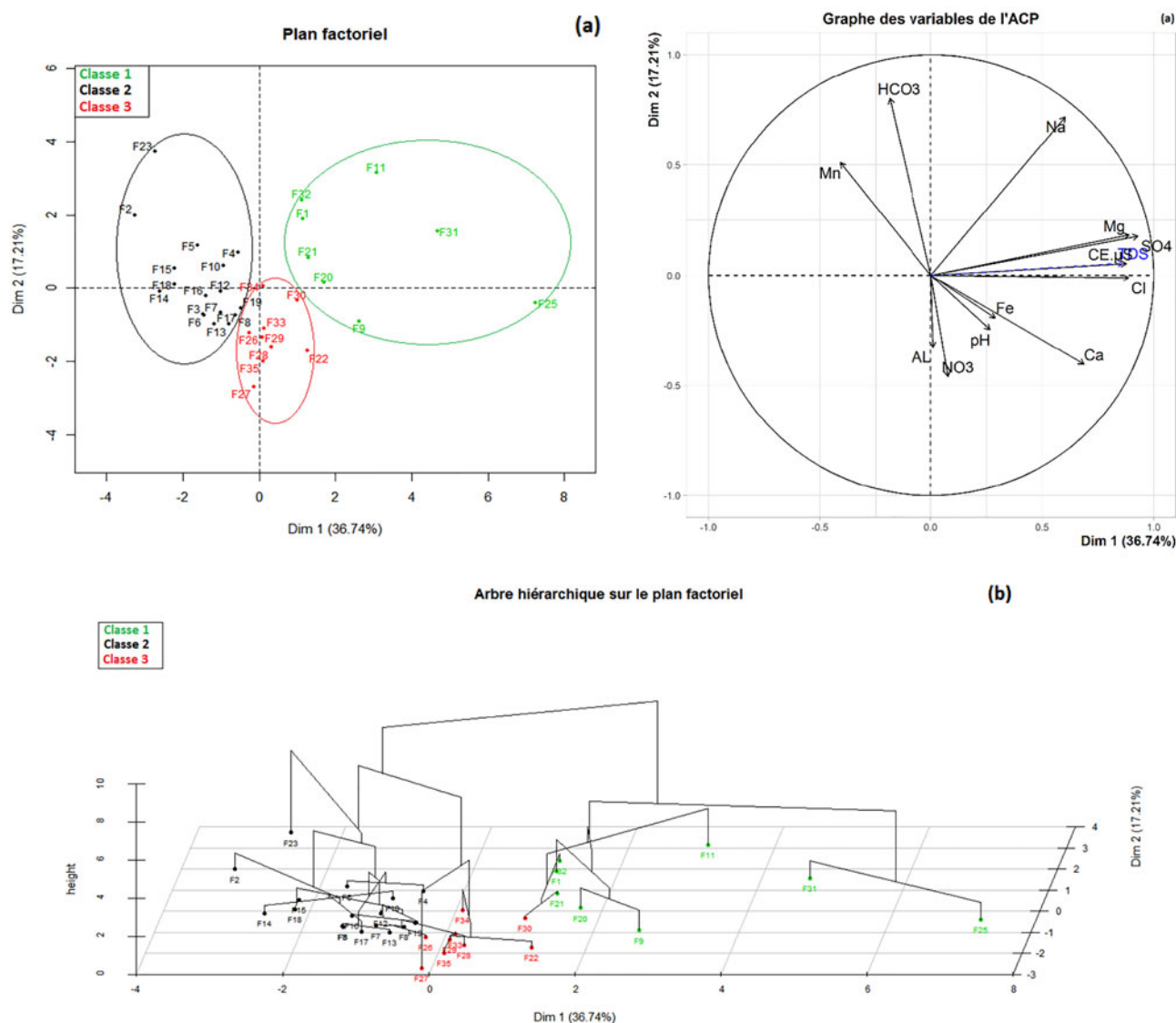


Figure 3 Statistical analysis: (a) principal component analysis; (b) the ascending hierarchical clustering of Remila waters (Khenchela).

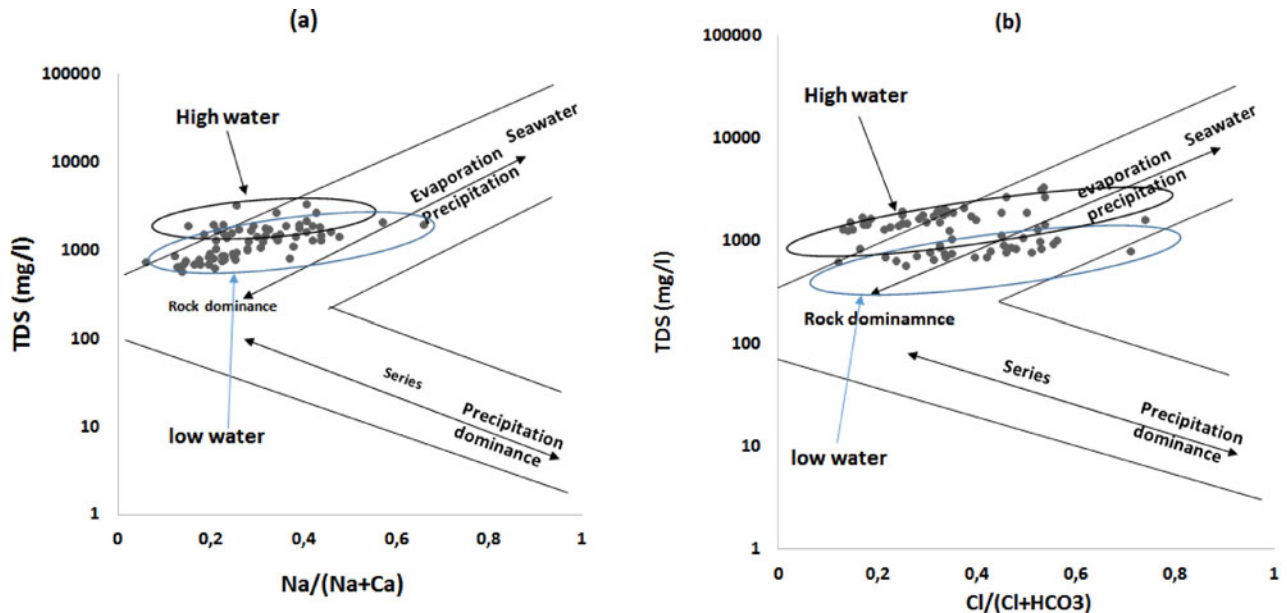


Figure 4 Gibbs Diagrams of Remila groundwater.

the water, especially for sulphate, which is closely linked to TDS. The second group consists of HCO_3^- , Fe^{2+} and pH, which contributes only weakly to water mineralisation. The third group, represented by manganese (Mn^{2+}) and lithium (Li^+), is more variable and has a marginal effect on the water mineralisation.

The results provided by the PCA of the individual samples and AHC are in perfect agreement, since they demonstrated that water mineralisation is dominated by sulphate; in addition, the typology of the water samples can be represented by three facies.

2.3. Groundwater mineralisation processes

A statistical relation between two or more variables is indicated by correlations. The results show that SO_4^{2-} , Mg^{2+} , Cl^- , Ca^{2+} , Na^+ , HCO_3^- , Sr^{2+} , K^+ ions and TDS are significantly correlated, indicating the contribution of these elements to groundwater salinity and suggesting that evaporitic rocks dissolution may be a common source of mineralisation. Such results require geochemical calculations of speciation solubility in order to identify the dominant processes, which influence Remila plain groundwater hydro-geochemistry.

2.3.1. Water-rock interaction. Gibbs diagrams are widely used to evaluate the functional source of dissolved ions that control water chemistry such as precipitation dominance, rock weathering and evaporation dominance (Gibbs 1970; Dhanwinder-singh 2011; Varol & Davraz 2014; Masoud *et al.* 2018). The chemical data are plotted in a semi-logarithmic dispersion of TDS values versus anions ($Cl^-/(Cl^- + HCO_3^-)$) and cations ($Na^+/(Ca^{2+} + Na^+)$); all concentrations of ionic values are expressed in meq/l (Fig. 4).

As shown by the data projected in the Gibbs diagrams, the majorities of the groundwater samples of the two seasons are located in the predominantly rocky zone, but also have a tendency towards the zone of evaporation and precipitation. Therefore, the mineralisation of our water is controlled by the dissolution of evaporitic rocks and is affected by Sabkha saline water, which is subjected to intense evaporation followed by salt precipitation, which will affect the quality of our waters, particularly in the northeastern part of the area.

Most of the results show an excessive concentration of cations versus anions, indicating that another source of these cations should be possible, such as ion exchange. Nevertheless, Schoeller (1965) proposed a chloro-alkaline index (CAI) that can be used

to determine the degree of ion exchange reactions between the aquifer substratum and groundwater. It is a commonly used tool for the recognition of dominant processes of ion exchange in groundwater (Abu-alnaeem *et al.* 2018; Ayadi *et al.* 2018). The CAI is calculated using the equation $(Cl^- - (Na^+ + K^+)) / Cl^-$; the values are in meq/l. If the CAI values tend to decrease (negative), this indicates a dominance of the basic processes of ion exchange, where Ca^{2+} and Mg^{2+} are adsorbed on the substratum and K^+ and Na^+ are released in water. Whereas, if the CAI index values tend to increase (positive), this implies a dominance of the processes of reverse ion exchange, where K^+ and Na^+ are adsorbed on the substratum and Ca^{2+} and Mg^{2+} are released in water. However, if the CAI values are close to zero and show a balance, this implies the absence of an exchange process.

The calculated CAI in the study area shows positive values for most groundwater samples (68%); this indicates the dominance of the reverse exchange process in which Ca^{2+} , Mg^{2+} of the aquifer substratum is released and Na^+ , K^+ are adsorbed. Although just 26% of the samples have values close to zero, which imply equilibrium and indicates an absence of ion exchange, they have been found in the southeastern part of the region. Nevertheless, only 2% of the samples show negative values, which indicates the dominance of the processes of direct ion exchange, thus releasing Na^+ , K^+ from the aquifer substratum and fixing Ca^{2+} , Mg^{2+} from the water, they have been found in the north-eastern part of the region.

The saturation index (SI) is a commonly used tool to identify water-rock interactions, as well as the hydro-chemical processes that control groundwater chemistry (Parkhurst & Appelo 1999; Rina *et al.* 2013; Ayadi *et al.* 2018). The SI describes the level of saturation of the water towards the various minerals: when $SI = 0$, the minerals in the solution are in equilibrium; when $SI < 0$, the solution is under-saturated, which promotes the dissolution of minerals, while $SI > 0$ indicates the saturation of the solution that contributes to the precipitation of the minerals (Appelo 1994). The mineral SI was calculated using the PHREEQC geochemical modelling program (Parkhurst & Appelo 1999), and using the following equation:

$$SI = \log\left(\frac{IAP}{K_t}\right) \quad (1)$$

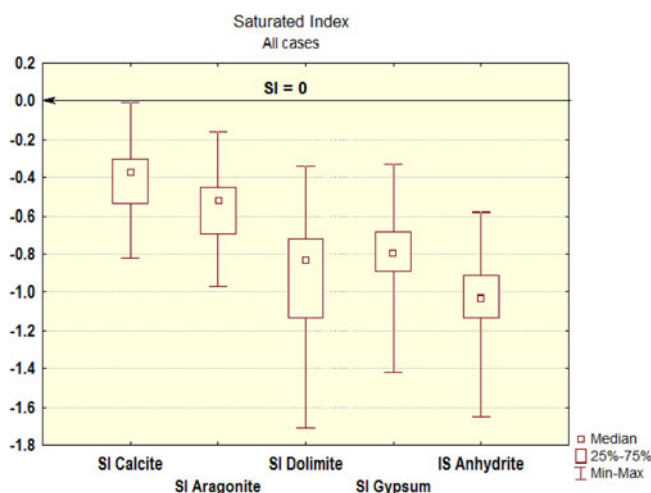


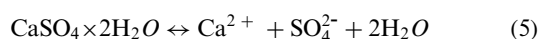
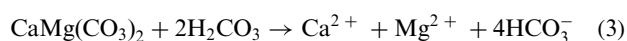
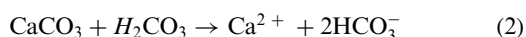
Figure 5 Saturation index (SI) variability diagrams in groundwater at Remila (Khenchela).

where IAP = ion activity product and K_i = equilibrium solubility constant.

The results show that the area's groundwater is undersaturated with respect to gypsum, anhydrite and dolomite ($SI < 0$), which indicates that these minerals should be dissolved in our water. Although the groundwater is slightly undersaturated with calcite and aragonite, this means that they are in a state of equilibrium, but these minerals can still influence the chemical composition of the water (Fig. 5).

2.3.2. Dissolution/precipitation of carbonate and evaporite minerals. In order to gain insight into the geochemical mechanisms and processes that contribute to water mineralisation, ionic ratios are commonly used.

In the dissolution of carbonate and gypsum, hydro-chemical results show that the predominant salt elements are SO_4^{2-} , Mg^{2+} , Ca^{2+} and HCO_3^- ; this appears to be the cause of dissolved evaporites. Consequently, dissolving carbonate and gypsum minerals is a crucial process in water mineralisation (Eqs 2–5) (Edmunds *et al.* 1982):



Generally, carbonate dissolution is identified by the Ca^{2+}/HCO_3^- ratio in meq/l. If the dissolution of calcite affects the water, the values in this ratio are close to the dissolution line (1:1), but if the ratio values are close to 0.5 this indicates that the dissolution of dolomite is the source of those ions. When the values exceed 1, this indicates another source of those ions (Abu-alnaeem *et al.* 2018). Based on the projection results of the water points (Fig. 6a), we notice that most of the points are above the dissolution line (1:1), suggesting an excess of Ca^{2+} versus HCO_3^- . This confirms that other processes such as gypsum dissolution and ion exchange affect the concentration of Ca^{2+} ions in water. While there are only two water points below the dissolution line (1:1), which indicates a deficit of Ca^{2+} by supplying HCO_3^- , this can be explained by calcite and/or dolomite precipitation and ion exchange favoured by the saline intrusion of the Sabkha water. The dissolution of calcite and dolomite in groundwater can be assessed by using another ratio: Ca^{2+}/Mg^{2+} . If the ratio values

are close to or equal to 1, the water has been affected by the dissolution of the dolomite; on the other hand, if the ratio values are between 1 and 2, the water has been affected by the dissolution of the calcite; and finally, when the ratio values exceed 2, the water has been affected by the dissolution of the silicate minerals (Lakshmanan *et al.* 2003). According to the calculated results, the majority of the samples (64%) have ratios between 1 and 2, while 23% of the samples have ratios close to or equal to 1, which suggests that the source of Ca^{2+} ions in most water comes from the dissolution of calcite and dolomites, whereas some ions are affected by the process of ion exchange.

Within the dissolution of gypsum, the ratio Ca^{2+}/SO_4^{2-} (meq/l) is widely used to assess the dissolution of gypsum in water. The projection of the results in the Ca^{2+} versus SO_4^{2-} binary diagram (Fig. 6c) shows that most groundwater samples are near to the gypsum dissolution line (1:1), which indicates that gypsum is an important source of Ca^{2+} in the area's water. Although other samples are above the dissolution line, this suggests a deficit of Ca^{2+} , which can be explained by inverse ion exchange involvement, by the Ca^{2+} adsorption and Na^+ release, while this has been favoured by the saline intrusion (Sabkha) in the northeastern part of the area. However, according to Appelo (1994), the saline intrusion induces dolomitisation, and this will cause Ca^{2+} ion fixation and the release of Mg^{2+} ions. On the other hand, some water points show an excess of Ca^{2+} relative to SO_4^{2-} , with a surplus of Ca^{2+} followed by a deficit of Na^+ , which confirms the involvement of these two ions in ion exchange. The Sr^{2+}/Ca^{2+} ratio of molar concentrations also helps us to determine the source of sulphate in groundwater (Hsissoua *et al.* 1996; Edmunds *et al.* 2003). The calculated ratio results (Fig. 6d, f) showed that all water points had values greater than 5‰, indicating the effect of gypsiferous formations on the presence of strontium. This result is completely consistent with the types of facies found in the study area where sulphates are most predominant.

In the dissolution of halite, the results of the sampled water suggest a high Na^+ and Cl^- content, and halite dissolution is often the source of these ions. A binary diagram of Na^+ versus Cl^- was used to identify the source of these ions (Fig. 6e). The distribution of water points in the diagram shows the presence of three groups of water: the first group is the point close to the halite dissolution line (1:1), which means that the water is influenced by the dissolution of the halite; often it is the water in the southeastern part of the region close to the recharge area. The second group was represented by most of the water points below the line (1:1), indicating a deficit in Na^+ compared to Cl^- , revealing that the water is influenced by processes other than halite dissolution, such as reverse ion exchange with Na^+ adsorption and the release of Mg^{2+} and/or Ca^{2+} from the substratum. The third group includes the water points above the halite dissolution line (1:1), which are characterised by an excess of Na^+ compared to Cl^- ; they are located in the northeastern part of the study area, where these waters are overloaded with Na^+ under the influence of saline intrusion (Sabkha water), and this could be favoured by the intensive exploitation of the aquifer, which lowered the piezometric level of the aquifer followed by the advancement of the Sabkha saline water.

Within the cationic exchange, wide fluctuations in the concentration of major ions occur by various processes; ion exchange often causes changes or reversals of groundwater cationic concentrations. However, studying the relationship between $Ca^{2+} + Mg^{2+}$ and $HCO_3^- + SO_4^{2-}$ will allow us to identify the processes that influence groundwater mineralisation. The binary diagram of $Ca^{2+} + Mg^{2+}$ versus $HCO_3^- + SO_4^{2-}$ (Fig. 7a) shows a projection of the water points around the line (1:1). Generally, the water points, which are close to or on the line (1:1), are under the influence of the dissolution of calcite, dolomite, anhydrite and gypsum (Hamzaoui-Azaza *et al.* 2013; Hassen *et al.*

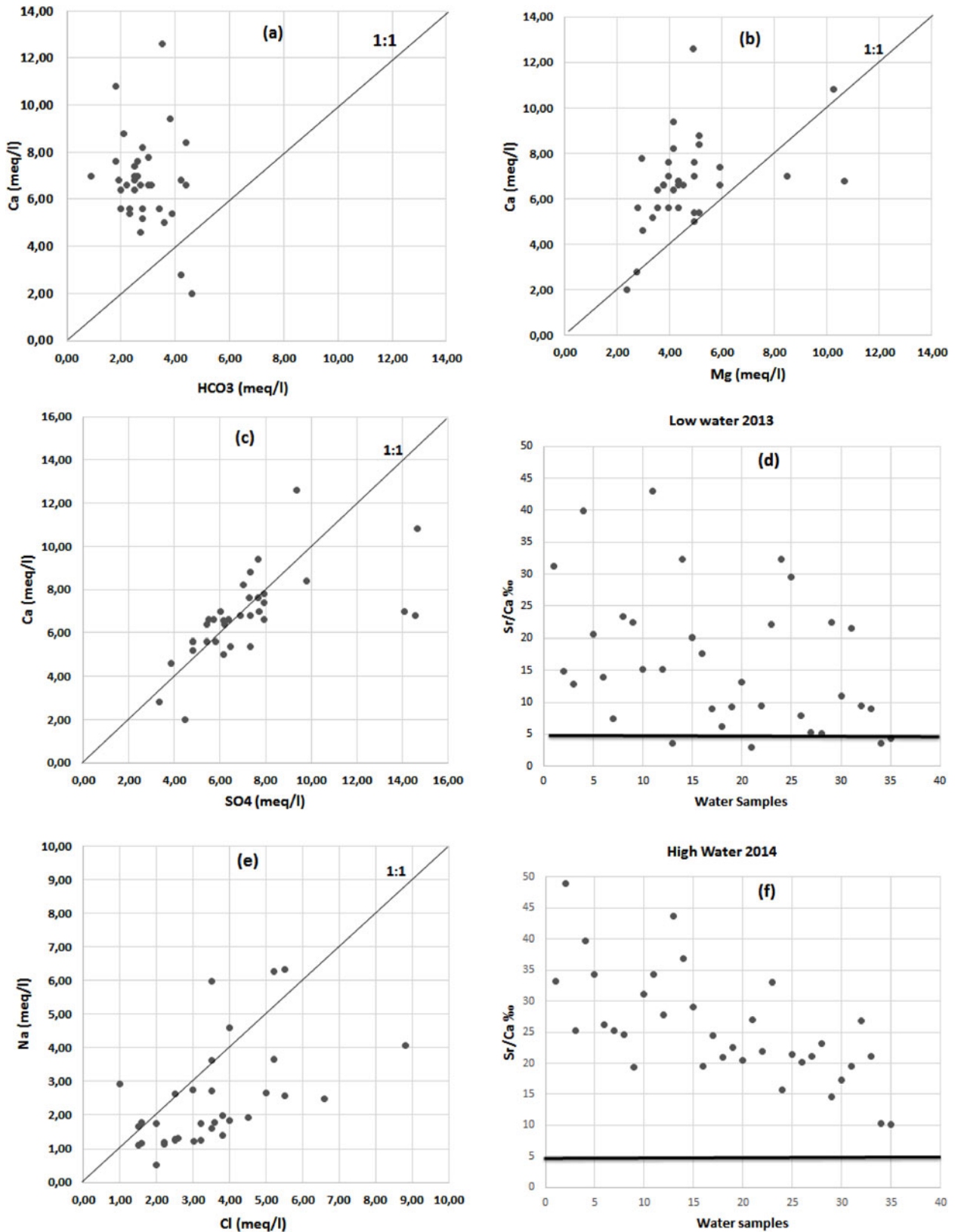


Figure 6 Scatter plots of (a) Ca²⁺ versus HCO₃⁻; (b) Ca²⁺ versus Mg²⁺; (c) Ca²⁺ versus SO₄²⁻; (d) Sr²⁺/Ca²⁺ ratio of low waters; (e) Na⁺ versus Cl⁻; (f) Sr²⁺/Ca²⁺ ratio of high waters of the Remila groundwater samples.

2016). While water points that are above the line (1:1) indicate an excess of Ca²⁺ + Mg²⁺, they are generally influenced by ion exchange (Tlili-Zrelli *et al.* 2013). In fact, the water points below the line (1:1) indicate a deficit of Ca²⁺ + Mg²⁺; this decrease in concentration is attributed to reverse ion exchange (Rina *et al.* 2013). The results of the water point projections in the diagram (Fig. 7a) show that most water points are above

the line (1:1) due to excess Ca²⁺ + Mg²⁺ and this indicates that reverse ion exchange is a very abundant geochemical process in the aquifer. The water points located in the northeastern part near Sabkha (salt water) are projected below the line (1:1), suggesting a deficit in Ca²⁺ + Mg²⁺, which indicates that the water in this part of the study area is under the influence of ion exchange and saline intrusion.

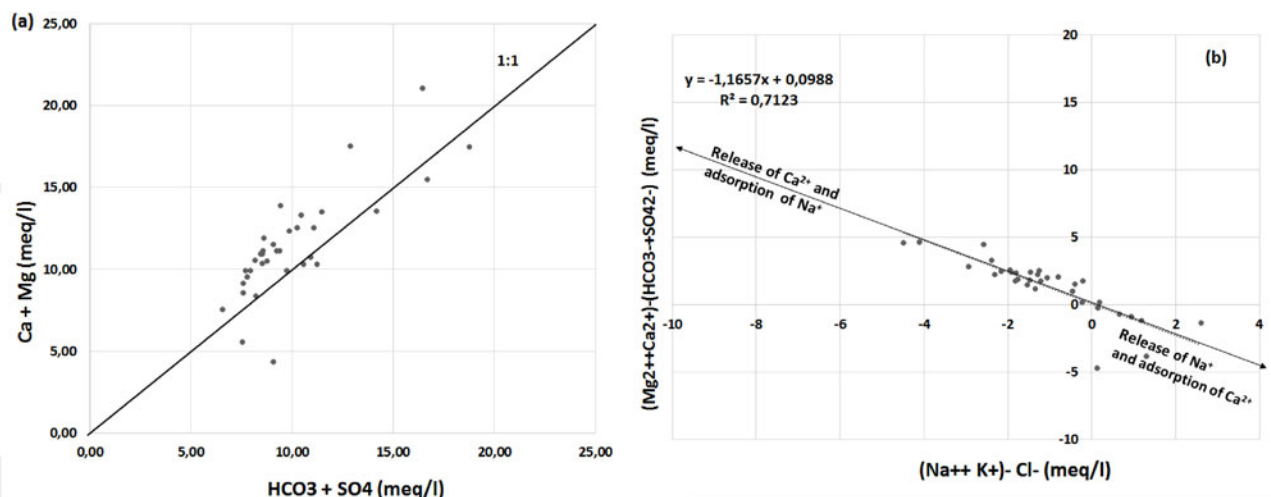


Figure 7 Scatter plots of (a) $\text{Ca}^{2+} + \text{Mg}^{2+}$ versus $\text{HCO}_3^- + \text{SO}_4^{2-}$; (b) $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$ versus $(\text{Na}^+ + \text{K}^+) - \text{Cl}^-$ in (meq/l) of the Remila groundwater samples.

For further confirmation that the ion exchange process affects the hydrochemistry of Remila groundwater, another diagram is generated – this diagram has been widely used in various studies (García & Blesa 2001; Bekkoussa *et al.* 2013; Kraiem *et al.* 2015). The diagram $(\text{Ca}^{2+} + \text{Mg}^{2+}) - (\text{HCO}_3^- + \text{SO}_4^{2-})$ versus $(\text{Na}^+ + \text{K}^+) - \text{Cl}^-$ in (meq/l) (Fig. 7b) shows that the ion exchange process may be a feature of the study area, since most water points follow a straight line ($R^2 = 0.72$) with a slope of 1.08, suggesting that the cations Ca^{2+} , Mg^{2+} , Na^+ and K^+ are integrated into the cation exchange reactions. The sample distributions show that the majority of the saline groundwater in the western part of the area has migrated in the same direction, with a rise in Ca^{2+} and Mg^{2+} concentrations and a decrease in Na^+ and K^+ concentrations, indicating that water mineralisation is affected by rock dissolution accompanied by an ion exchange. Although water points located in the NE parts of the area are characterised by a high concentration of sulphate, they show a slight decrease in Ca^{2+} and Mg^{2+} , whereas significant increases in Na^+ and K^+ are observed. Such findings can be explained by the effect of reverse ion exchange in which Na^+ is released from the substratum and the Ca^{2+} are adsorbed, which is favoured by the saline intrusion of Sabkha saline water (Appelo 1994). These results confirm that two main processes control our water hydrochemistry: dissolution of evaporitic rocks and ion exchange.

3. Conclusion

The unmanaged extraction of groundwater, low and sporadic annual rainfall and the land endorheic have created an inversion of the hydraulic gradient and, thus, an increase in the salinity of the groundwater and a change in the hydro-chemical facies of the groundwater of Remila plain. In order to identify the main salinisation processes and the origin of the degradation of the quality of the aquifer system in the study area, an integrated statistical hydro-geochemical approach has been applied. The results show a significant salinity variation (TDS) of 568 to 1586 mg l^{-1} with an average of 906.3 mg l^{-1} after the dry season, and 1250 to 3270 mg l^{-1} with an average of 1822.16 mg l^{-1} after the wet season, indicating that precipitation during the rainy season was also a major source of dissolved species in the groundwater. Spatial variation suggests that three facies dominate the aquifer: $\text{SO}_4\text{-Cl-Ca}$ saline water in the NE, $\text{HCO}_3\text{-Ca-Mg}$ water in the SE is of decent quality and $\text{SO}_4\text{-Cl-Ca-Mg}$ moderately saline water represents

most of the water, which mainly results from water–rock interactions, such as evaporite and carbonate mineral dissolution and cation exchange reactions.

Statistical analysis reveals a normal distribution of the data, and the Variance Coefficient (CV) points out that the measured parameters are mainly influenced by environmental factors, especially during the rainy season, whereas the overall direct anthropogenic effects in the study area were minor. The relationship between the physicochemical parameters using the Pearson correlation showed that there seemed to be common sources for the variables, which is evaporite dissolution. Through a multivariate statistical analysis using PCA and HCA, three groups of water were identified: (1) saline water with SO_4^{2-} dominance (17%), where $\text{TDS} > 1000 \text{ mg l}^{-1}$; (2) moderately saline water with HCO_3^- dominance (17%); and (3) moderately saline water with mixed facies (66%).

The coupled use of major and minor ion chemistry has made it possible to identify the geochemical processes that take place in Remila aquifer. Interesting processes have been identified, including the dissolution and/or precipitation of evaporitic rocks (calcite, gypsum, halite and dolomite), often accompanied by cation exchange or reverse cation exchange. In addition, another process (saline water intrusion) has been identified in the northeastern part near the Sabkha, which is generated by the intensive exploitation of the aquifer by farmers. This process may pose a long-term water quality problem due to the reverse exchange in groundwater (sodium-enriched water with its problems). Unless current levy rates do not decrease, this process could represent a long-term problem for the region's groundwater quality due to reverse exchange (with sodium enrichment of the water and its impact on environmental degradation).

The results of this study indicate that the integrated statistical and hydro-geochemical approach can be a very effective tool to identify the processes that control groundwater and the different sources of salinisation in water. Therefore, the results of this study can be used as a conceptual platform for future research. In addition, the improvement of the hydro-geochemical knowledge of Remila plain aquifer system may lead to the implementation of a series of measures that aim towards making progress on groundwater management. They can be summarised as follows: the reduction of groundwater withdrawals (particularly for irrigation) by the use of treated wastewater or/and dam construction in the S of the region; the relocation of pumping wells (particularly in the northeastern part of the area) to other aquifer sectors less vulnerable to salinisation; and the development of a

monitoring network. This study shows that to achieve sustainable exploitation of groundwater, without deteriorating its quality, it is necessary to have prior hydro-geochemical knowledge of the aquifer that is to be exploited. Unconfined aquifers such as the Quaternary, found in semi-arid areas with short renewal periods, are very vulnerable to exploitation. During periods of drought, the pumping of groundwater can generate rapid draw-downs at piezometer levels – a situation that favours the intrusion of salt water from Sabkha.

4. References

- Abu-alnaeem, M. F., Yusoff, I., Ng, T. F., Alias, Y. & Raksmei, M. 2018. Assessment of groundwater salinity and quality in Gaza coastal aquifer, Gaza Strip, Palestine: an integrated statistical, geostatistical and hydrogeochemical approaches study. *Science of the Total Environment* **615**, 972–89.
- Ahoussi, E. K., Soro, N., Kouassi, A. M., Soro, G., Blaise, Y. & Pacôme, S. 2010. Application des méthodes d'analyses statistiques multivariées à l'étude de nappes phréatiques de la ville d'Abidjan. **4**, 1753–65.
- Akouvi, A., Dray, M., Violette, S., de Marsily, G. & Zuppi, G. M. 2008. The sedimentary coastal basin of Togo: example of a multilayered aquifer still influenced by a palaeo-seawater intrusion. *Hydrogeology Journal* **16**, 419–36.
- Aouidane, L. 2017. *Origines de la salinisation des eaux et des sols d'une zone à climat semi-aride: Cas de Remila (W. Khenchela)*. Thèse de Doctrat. Université Mohamed Khider Biskra. 220 p.
- Aouidane, L. & Belhamra, M. 2017. Hydrogeochemical processes in the Plio-Quaternary Remila aquifer (Khenchela, Algeria). *Journal of African Earth Sciences* **130**, 38–47.
- Appelo, C. A. J. 1994. Cation and proton exchange, pH variations, and carbonate reactions in a freshening aquifer. *Water Resources Research* **30**, 2793–805.
- Ayadi, Y., Mokadem, N., Besser, H., Redhaouia, B., Khelifi, F., Harabi, S., Nasri, T. & Hamed, Y. 2018. Statistical and geochemical assessment of groundwater quality in Statistical and geochemical assessment of groundwater quality in Tebourouk area (Northwestern Tunisian Atlas). *Environmental Earth Sciences* **77**, 349.
- Bekkoussa, B., Jourde, H., Batiot-Guilhe, C., Meddi, M., Khaldi, A. & Azzaz, H. 2013. Origine de la salinité et des principaux éléments majeurs des eaux de la nappe phréatique de la plaine de Ghriiss, Nord-Ouest algérien. *Hydrological Sciences Journal* **58**, 1111–27.
- Bouderbala, A. 2015. Groundwater salinization in semi-arid zones: an example from Nador plain (Tipaza, Algeria). *Environmental Earth Sciences* **73**, 5479–96.
- Bouzourra, H., Bouhlila, R. & Elango, L. et al. 2015. *Characterization of mechanisms and processes of groundwater salinization in irrigated coastal area using statistics, GIS, and hydrogeochemical investigations*. *Environmental Science and Pollution Research* **22**, 2643–60. <https://doi.org/10.1007/s11356-014-3428-0>
- Brovelli, A., Carranza-Diaz, O., Rossi, L. & Barry, D. A. 2011. Design methodology accounting for the effects of porous medium heterogeneity on hydraulic residence time and biodegradation in horizontal subsurface flow constructed wetlands. *Ecological Engineering* **37**, 758–70.
- Capaccioni, B., Didero, M., Paletta, C. & Didero, L. 2005. Saline intrusion and refreshing in a multilayer coastal aquifer in the Catania Plain (Sicily, Southern Italy): dynamics of degradation processes according to the hydrochemical characteristics of groundwaters. *Journal of Hydrology* **307**, 1–16. doi.org/10.1016/j.jhydrol.2004.08.037.
- Cassardo, C. & Jones, J. A. A. 2011. Managing water in a changing world. *Water* **3**, 618–28.
- C.G.G. 1969. *Prospection Géophysique de la plaine de Remila (Khenchela)*. Coupes transversales. Département Trav. Publique Batna.
- C.P.H. 1977. *Proposition de réalisation d'étude et projets d'aménagement hydro agricole de la plaine de Remila Rapport de Consortium Projetum-HIDROESB, Rio de Janeiro Janvier*. 100 p.
- Dechesne, M., Barraud, S. & Bardin, J. P. 2004. Indicators for hydraulic and pollution retention assessment of stormwater infiltration basins. *Journal of Environmental Management* **71**, 371–80.
- D.H.W.K. 1984. *Schema Directeur de planification et d'aménagement. Services de production et d'aménagement*. Direction de l'Hydraulique de la Wilaya de Khenchela. 27 p.
- Edmunds, W. M., Bath, A. H. & Miles, D. 1982. Hydrochemical evolution of the East Midlands Triassic sandstone aquifer, England. *Geochimica et Cosmochimica Acta* **46**, 2069–81.
- Edmunds, W. M., Guendouz, A. H., Mamou, A., Moulla, A., Shand, P. & Zouari, K. 2003. *Groundwater evolution in the Continental Intercalaire aquifer of southern Algeria and Tunisia: trace element and isotopic indicators*. **18**, 805–22.
- Farid, I., Trabelsi, R., Zouari, K. & Beji, R. 2013. *Geochemical and isotopic study of surface and groundwaters in Ain Bou Mourra basin, central Tunisia*. *Quaternary International* **303**, 210–27.
- Frape, S. K., Fritz, P. & McNutt, R. H. 1984. Water-rock interaction and chemistry of groundwaters from the Canadian shield. *Geochimica et Cosmochimica Acta* **48**, 1617–27.
- García, G.M., Hidalgo del, V.M. & Blesa, M.A. (2001). *Geochemistry of groundwater in the alluvial plain of Tucumán province, Argentina*. *Hydrogeology Journal* **9**, 597–610. <https://doi.org/10.1007/s10040-001-0166-4>
- Ghabayen, S. M. S., Mckee, M. & Kemblowski, M. 2006. Isotopic ratios for identification of salinity sources and missing data in the Gaza aquifer. *Journal of Hydrology*, **318**, 360–73. doi.org/10.1016/j.jhydrol.2005.06.041
- Ghesquière, O., Walter, J., Chesnaux, R. & Rouleau, A. 2015. Journal of hydrology: regional studies scenarios of groundwater chemical evolution in a region of the Canadian shield based on multivariate statistical analysis. *Journal of Hydrology: Regional Studies* **4**, 246–66.
- Gibbs, R. J. 1970. Mechanisms controlling world water chemistry. *Science (New York, N. Y.)* **170**, 1088–90.
- Gil-márquez, J. M., Antonio, J. & Andreo, B. 2017. Geochemical evolution of groundwater in an evaporite karst system: brujuelo area (jaén, S Spain). *Procedia Earth and Planetary Science* **17**, 336–39.
- Grillot, J. C. & Schoeller, M. 2015. *Exemple d'approche pluridisciplinaire dans la caractérisation d'eaux thermales carbo-gazeuses. A pluridisciplinaire approach to carbonic and groundwater survey*. *Journal of Water Science* **2**, 211–28.
- Hamzaoui-Azaza, F., Tlili-Zrelli, B., Bouhlila, R. & Gueddari, M. 2013. An integrated statistical methods and modelling mineral-water interaction to identifying hydrogeochemical processes in groundwater in Southern Tunisia. *Chemical Speciation and Bioavailability* **25**, 165–78.
- Hassen, I., Hamzaoui-Azaza, F. & Bouhlila, R. 2016. Application of multivariate statistical analysis and hydrochemical and isotopic investigations for evaluation of groundwater quality and its suitability for drinking and agriculture purposes: case of Oum ali-thelepte aquifer, central Tunisia. *Environmental Monitoring and Assessment* **188**, 2–20.
- Hosseini, S. Z., Kappas, M., Bodaghabadi, M. B., Chahouki, M. A. Z. & Khojasteh, E. R. 2014. Comparison of different geostatistical methods for soil mapping using remote sensing and environmental variables in Poshtkouch rangelands, Iran. *Polish Journal of Environmental Studies* **23**, 737–51.
- Hsissoua, Y., Chauvea, P., Maniaa, J., Manginb, A., Bakalowicz, M. & Gaiz, A. 1996. *Characterization of the groundwaters of the Turoonian catchment of Tadla (Morocco) by the concentration ratios of Sr²⁺/Ca²⁺*. **183**, 445–51. doi.org/10.1016/0022-1694(95)03009-3
- Kerry, R. & Oliver, M. A. 2007. Determining the effect of asymmetric data on the variogram. I. Underlying asymmetry. *Computers and Geosciences* **33**, 1212–32.
- Kharroubi, A., Tlahigue, F., Agoubi, B., Azri, C. & Bouri, S. 2012. Hydrochemical and statistical studies of the groundwater salinization in Mediterranean arid zones: case of the Jerba coastal aquifer in southeast Tunisia. *Environmental Earth Sciences* **67**, 2089–100.
- K.M.S. 2014. *les donnees climatiques de la wilaya de Khenchela* (S. M. de la W. de Khenchela (ed.); Service de).
- Kraiem, Z., Zouari, K., Bencheikh, N. & Agoun, A. 2015. *Processus de minéralisation de la nappe du Plio- Quaternaire dans la plaine de Segui-Zograta (Sud- Ouest tunisien)*. *Hydrological Sciences Journal* **60**, 534–48.
- Kuldip-Singh, Hundal, H.S. & Dhanwinder, S. 2011. *Geochemistry and assessment of hydrogeochemical processes in groundwater in the southern part of Bathinda district of Punjab, northwest India*. *Environmental Earth Science* **64**, 1823–33.
- Laffitte, R. 1939. *Etude géologique de l'Aures Bull. Serv. Géol. de L'Algérie*. 1° série.
- Lakshmanan, E., Kannan, R. & Senthil Kumar, M. 2003. Major ion chemistry and identification of hydrogeochemical processes of ground water in a part of Kancheepuram district, Tamil Nadu, India. *Environmental Geosciences* **10**, 157–66.
- Li, J., Wang, Y. & Xie, X. 2016. Science of the Total Environment Cl/ Br ratios and chlorine isotope evidences for groundwater salinization and its impact on groundwater arsenic, fluoride and iodine enrichment in the Datong basin, China. *Science of the Total Environment*, **The** **544**, 158–67.
- Masoud, A. A., El-horiny, M. M., Atwia, M. G. & Gemail, K. S. 2018. Journal of African Earth Sciences Assessment of groundwater and soil quality degradation using multivariate and geostatistical analyses, Dakhla Oasis, Egypt. *Journal of African Earth Sciences* **142**, 64–81.
- Oliver, M. A. 2010. *Geostatistical Applications for Precision Agriculture* (M. A. Oliver (ed.); Springer D). Springer Science + Business Media B.V. 2010.

- Oliver, M. A. & Webster, R. 2014. A tutorial guide to geostatistics: computing and modelling variograms and kriging. *Catena* **113**, 56–69.
- Parkhurst, D. L. & Appelo, C. A. J. 1999. *USER'S GUIDE TO PHREEQC (VERSION 2)—A COMPUTER PROGRAM FOR SPECIATION, AND INVERSE GEOCHEMICAL CALCULATIONS* (U. S. D. O. T. INTERIOR (ed.); Hydrochemi, Issue Version 2). U.S. Geological Survey.
- Pazand, K., Hezarkhani, A., Ghanbari, Y. & Aghavali, N. 2012. *Geochemical and quality assessment of groundwater of Marand Basin, East Azarbaijan Province, northwestern Iran. Environmental Earth Science* **67**, 1131–43. doi.org/10.1007/s12665-012-1557-7
- Piper, A. M. 1944. *A graphic procedure in the geochemical interpretation of water analyses. Transactions of the American Geophysical Union* **25**, 914–23.
- Pisinaras, V., Tsihrintzis, V. A., Petalas, C. & Ouzounis, K. 2010. Soil salinization in the agricultural lands of Rhodope district, northeastern Greece. *Environmental Monitoring and Assessment* **166**, 79–94.
- Rina, K., Singh, C. K., Datta, P. S., Singh, N. & Mukherjee, S. 2013. Geochemical modelling, ionic ratio and GIS based mapping of groundwater salinity and assessment of governing processes in Northern Gujarat, India. *Environmental Earth Sciences* **69**, 2377–91.
- Rodier, J., Legube, B., Merlet & N. & Coll. 2009. *L'analyse de l'eau* (P. Dunod (ed.); 9e édition). Dunod Paris, 1959.
- Scanlon, B. R., Keese, K. E., Flint, A. L., Flint, L. E., Gaye, C. B., Edmunds, W. M. & Simmers, I. 2006. *Global synthesis of groundwater recharge in semiarid and arid regions. Hydrological Processes* **3370**, 3335–70.
- Schoeller, H. 1965. *La classification géochimique des eaux*. **2**, 16–24.
- Siebert, S., Burke, J., Faures, J. M., Frenken, K., Hoogeveen, J., Döll, P. & Portmann, F. T. 2010. Groundwater use for irrigation – a global inventory. *Hydrology and Earth System Sciences Discussions* **7**, 3977–4021.
- Tijani, M. N. 2004. *Evolution of saline waters and brines in the Benue-Trough, Nigeria. Applied Geochemistry* **19**, 1355–65. <https://doi.org/10.1016/j.apgeochem.2004.01.020>
- Tlili-Zrelli, B., Hamzaoui-Azaza, F., Gueddari, M. & Bouhlila, R. 2013. Geochemistry and quality assessment of groundwater using graphical and multivariate statistical methods. A case study: Grombalia phreatic aquifer (Northeastern Tunisia). *Arabian Journal of Geosciences* **6**, 3545–61.
- Van Breukelen, B. M., Appelo, C. A. J. & Olsthoorn, T. N. 1998. Hydrogeochemical transport modeling of 24 years of Rhine water infiltration in the dunes of the Amsterdam Water Supply. *Journal of Hydrology* **209**, 281–96.
- Varol, S. & Davraz, A. 2014. *Assessment of geochemistry and hydrogeochemical processes in groundwater of the Tefenni plain (Burdurlu Turkey). Journal Environmental Earth Science* **71**, 4657–73. <https://doi.org/10.1007/s12665-013-2856-3>
- Vila, J. M. 1977. *Notice explicative de la carte géologique, au 1/50.000, Touffana (feuille n 202)* (Sonatrach (ed.)).
- Viswanath, N. C., Dileep, P. G. & Ammad, K. K. 2015. Statistical analysis of quality of water in various water shed for Kozhikode City, Kerala, India. *Aquatic Procedia* **4**, 1078–85.
- Wang, Y. & Jiao, J. J. 2012. Origin of groundwater salinity and hydrogeochemical processes in the confined Quaternary aquifer of the Pearl River Delta, China. *Journal of Hydrology* **438–39**, 112–24.
- Yang, F., Zhang, G., Yin, X. & Liu, Z. 2011. Field-scale spatial variation of saline-sodic soil and its relation with environmental factors in Western Songnen Plain of China. *International Journal of Environmental Research and Public Health* **8**, 374–87.
- Yermani, M., Zouari, K., Michelot, J. L., Mamou, A. & Moumni, L. 2003. Geochemical approach to the functioning of the Gafsa North deep aquifer (central Tunisia). *Hydrological Sciences Journal* **48**, 95–108.
- Yidana, S. M., Ophori, D. & Banoeng-Yakubo, B. 2008. A multivariate statistical analysis of surface water chemistry data - the Ankobra Basin, Ghana. *Journal of Environmental Management* **86**, 80–87.
- Zektser, I. S. & Loaiciga, H. A. 1993. Groundwater fluxes in the global hydrologic cycle: past, present and future. *Journal of Hydrology* **144**, 405–27.
- Zewdu, S., Suryabhagavan, K. V. & Balakrishnan, M. 2017. Geo-spatial approach for soil salinity mapping in Sego Irrigation Farm, South Ethiopia. *Journal of the Saudi Society of Agricultural Sciences* **16**, 16–24.

MS received 16 March 2020. Accepted for publication 2 May 2021