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Geochemical and multivariate statistical study to assess the salinization origin of the Remila plain groundwater, Khenchela Algeria

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Keywords

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Explanation letter

Thank you for giving us the opportunity to submit a revised draft of the manuscript "Geochemical and multivariate statistical study to assess the salinization origin of the Remila plain groundwater, Khenchela Algeria" for publication in the Journal of Water and Land Development. We appreciate the time and effort that you and the reviewers dedicated to providing feedback on our manuscript and are grateful for the insightful comments on and valuable improvements to our paper. Attached is a letter in response to the comments of the reviewers with a detailed manuscript description.
Best thanks for your cooperation.
Kindly, cordially,

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The aquifer system of the Remila plain 250 km^2 (Khenchela, Algeria) is one of the semiarid regions where groundwater is heavily exploited for urban supply and irrigation. An integrated hydrogeochemical and statistical approach was performed by 70 water samples to identify the main processes and the origin of our waters' salinization. Chemical analyses indicate salinity values (TDS) ranging from 568 to 1586 $mg.l^{-1}$ with an average of 869 $mg.l^{-1}$, sulphate is the dominant ions, especially in the north and northeast part. While the identified chemical facies are : SO_4-Cl-Ca in the northeastern part, SO_4-Cl-Ca-Mg presents most waters and HCO_3-Ca-Mg in the southeastern part.

The statistical approach, which allowed us to group the waters into three groups using PCA and HCA; 1) saline waters (23%) (TDS > 1000 mg.l-1 and SO_4^{2-} dominance), 2) moderately saline waters (51%) with HCO_3^- dominance, 3) moderately saline waters (26%) with a mixed facies. The binary ion diagrams used suggest that the most hydrochemical processes are: evaporites dissolution and/or precipitation, accompanied by an exchange and/or reverse exchange of ions. Additionally, another process was detected in the northeastern part of the area; the saline intrusion of Sabkha waters, favored by intensive aquifer exploitation.

Keywords: Groundwater; Hydrogeochemistry; Statistics; Salinity; Remila.

1 Introduction

Freshwater resources account for only 3% of the planet's water and are mostly in frozen form, where groundwater accounts for only 30% of the world's freshwater [BENCHOKROUN 2008; CASSARDO and JONES 2011]. Although groundwater has become an important source of water supply for many countries domestic, industrial and agricultural sectors, and especially in arid and semi-arid regions [PEJMAN *et al.* 2009; BOUZOURRA *et al.* 2015; AOUIDANE 2017b]. In the southern Mediterranean regions, the Maghreb countries have become areas of intensive use of groundwater for agriculture and industry [SIEBERT *et al.* 2010]. In Algeria, 67% of irrigated lands are irrigated by groundwater [ZEKTSER and EVERETT 2004]. However, water quality plays a crucial role in plant growth, human health and the environment. Natural processes can lead to deterioration of groundwater quality, and some of these processes are exacerbated by human activities due to the over-exploitation of groundwater resources [RINA *et al.* 2013; MASOUD *et al.* 2018]. The identification of

geochemical processes in groundwater is, therefore, crucial for the sustainable management of these resources.

Salinization is one of the most common contaminants in water resources, especially in arid and semi-arid regions. Indeed, salinization 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]. Over the last few decades, salinization of groundwater has been the subject of considerable research [GIBBS 1970; YERMANI *et al.* 2003; PAZAND *et al.* 2012; AOUIDANE and BELHAMRA 2017a]. This problem can be attributed to natural and/or anthropogenic factors, such as; the interaction of water with rocks [FRAPE *et al.* 1984; GHESQUIÈRE *et al.* 2015], the intrusion of coastal saltwater or Sabkha water generated by excessive groundwater pumping [CAPACCIONIA *et al.* 2005], fossil seawater [TIJANI 2004; AKOUVI *et al.* 2008; FARID *et al.* 2013]. The anthropogenic intervention finally compounded local natural processes by saline water retention due to over-exploitation of groundwater, inadequate sewage disposal and intensive agricultural and industrial activities [ZEWDU *et al.* 2017]. Generally, groundwater salinization processes can be identified using many methods: such as geochemical analysis, with the use binary ratios of major and minor tracers [SANCHEZ-MARTOS *et al.* 2002; SCANLON *et al.* 2006; GIL-MÁRQUEZA *et al.* 2017], Isotopic tracers [CHANGKAKOTI *et al.* 1986; GHABAYEN *et al.* 2006; HASSEN *et al.* 2016] and including statistical analysis [KHARROUBI *et al.* 2012; VISWANATH *et al.* 2015; SUDHEER *et al.* 2017; MASOUD *et al.* 2018].

Like many arid and semi-arid areas, this general situation exists in the endorheic Remila basin, which is the subject of this study. Situated in northeastern Algeria, this area is limited to the north by the depression of Sabkha Garaat Etarf. Precipitation is rare, characterized by sporadic and random temporal and spatial variations, focus on short periods. This area is urbanizing with agricultural vocation, and the water supply comes mainly from groundwater. Therefore, it is important to understand the main processes that control the salinization of these waters, within the limits of improving water resource quality management in this region.

The main aim of this study is to identify factors that control groundwater salinity. An integrated approach between geological, hydrogeological, hydrochemical and statistical was used to (1) assessment of groundwater chemistry to highlight dominant groundwater mineralization processes (2) use statistical analyzes to identify distinct water groups and assess the correlation between different elements and factors of water hydrochemistry (3) and identify recharge areas and major sources of contamination. A better understanding of the sources of salinization and contamination of the Remila aquifer system (Khenchela) will then

serve as an important scientific basis for the study area's water resource planning and management.

2 Materials and Methods

2.1 Study area

The study area is part of the endorheic basin of Garaat Et Tarf. It is located in northeastern Algeria lies between the parallels 35°25' and 35°40' north latitudes, and 06°30' and 07°05' east longitudes, on an area of 250 km^2 with a flat topography where an altitude of 800 to 1000 m. The study area is surrounded to the south by the northern slope of the Aurès Mountains, which is the recharge area; to the north by the Djbel Fdjoudj mountain range and to the northeast by the depression Sabkha of Gareat Et Tarf (Fig. 1) [C.P.H. 1977]. The semi-arid climate of the region is characterized by annual precipitation less than 400 mm with an average annual temperature of 17 °C, the minimum and maximum temperatures of which were noted in January (6 °C) and in August (30 °C) respectively and with potential annual evapotranspiration of 1050 mm. Surface water in the area is scarce, and groundwater is the only source of water for urban and agricultural use.

2.1.1 Geological setting

From a geological point of view, the Remila region is located in a depression zone with a length of 50 to 60 km and an average width of 20 km. It represents as a whole, a floodplain of Mio-Pliocene and quaternary deposits transported by Streams, and then deposited in a sequence of floodplains due to stream flow regimes [LAFFITTE 1939; C.G.G. 1969]. The Cretaceous series surrounding the study area is composed of Middle Cretaceous (Aptian) or Upper Cretaceous (Cenomanian, Turonian, and Senonian), which are the most extensive on the south and north side. While in the north-west part, the Miocene is presented by a limestone-sandstone and limestone deposit (Burdigalian) which are arranged discordantly on the Cretaceous and the red Pontian marl. An endorheic saline depression (Sabkha Great Etart) of 200 km^2 occupies the eastern part of the plain [VILA 1977]. The study area's lithostratigraphy (Remila plain) is characterized by the development of recent Quaternary soils (Fig. 1).

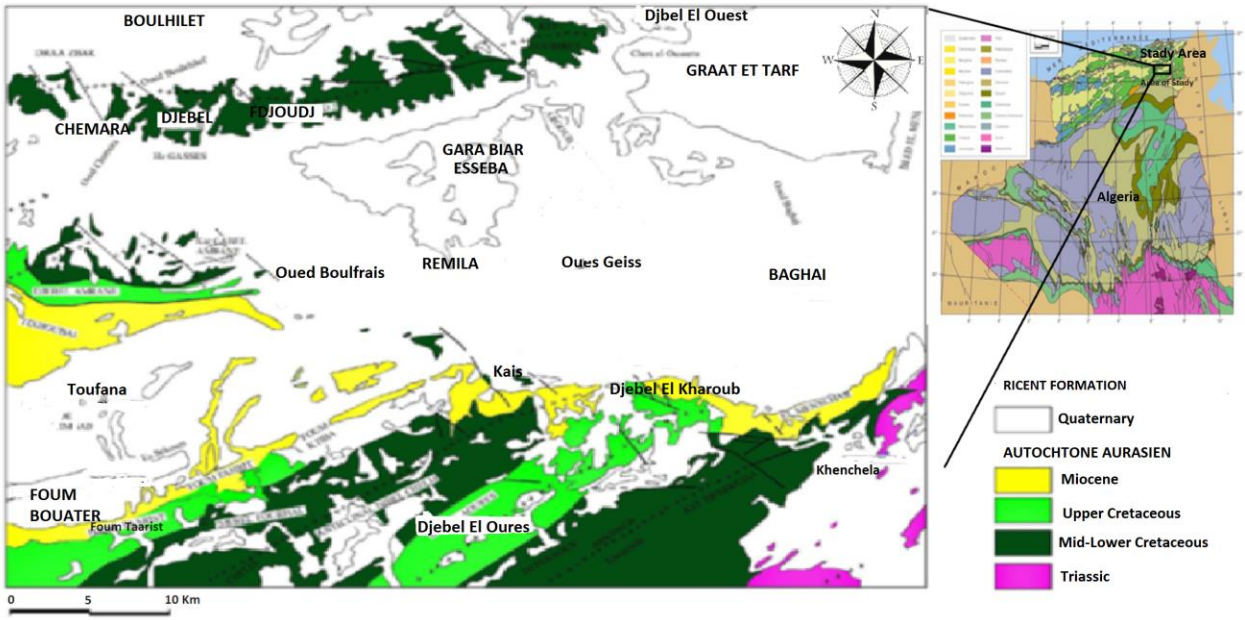

Fig. 1. Map showing location and geological formations of the study area

2.1.2 Hydrogeological setting

The hydrographic system distribution in the study area 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 Boulefreis Oued drains the entire area from its source to the southwest to discharge to the Sabkha in the northeast. Also, there are other less important streams; the Oued Baghai draining the eastern part, but the center of the area is drained by Oueds Maarouf and Oued Gueiss the streams flow is temporary and pours into a closed depression (Sabkha of Garaat Etarf) [D.H.W.K. 1984].

The Remila aquifer is housed in a sandy-marly limestone substratum of the Moi-Plio-Quaternary. The geochemical properties and groundwater recharge mode will generally depend on the aquifer's depth and lithostratigraphy. 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, housed in the alluvial filling of the plain [C.G.G. 1969]:

- Alluvial aquifers (Plio-Quaternaries): represent the largest regional groundwater resource occupying the Remila basin. They consist of coarse detrital elements, sand, gravel, and conglomerate, packed in a clay-loamy matrix and are the place for good water circulation.
- The Miocene aquifer, which extends along the southern edge of the basin with a synclinal shape defined under the quaternary recovery, is only of local interest and is therefore, less exploited. It's marine sandstone drowned in a large thickness of

greenish gravelly marls or gray-blue and is actually quite hard and low permeability rock.

- The quaternary lands of the western and central plains compose of several gross layers, well-developed sand, gravel, and conglomerates. Are less extensive and less wide in the southeastern section of the plains. Thus, this formation constitutes a permeable cover, allowing meteoric water to infiltrate, which due to its highlighting permeability plays an important hydrogeological role.

2.2 Sample collection

During two campaigns, groundwater sampling from 35 boreholes was carried out to identify the dominant hydrogeochemical processes in the Remila aquifer system. The first is collected in the dry period in December-October 2013 and the second is collected in the wet period from May-June 2014. We used the methods recommended by RODIER *et al.* [2016] in the sampling and analysis to minimize handling errors. Sampling and measurements were carried out in functional supply boreholes. The borehole water was pumped out two to three times before sampling. Regular monitoring of the electrical conductivity was checked in parallel until the values were stable.

The samples taken from the water are untreated and raw. For each sample, water was taken from a 1 liter pre-rinsed polyethylene bottle and filtered through a 0.45 µm membrane filter. The bottles were filled to minimize exposure to air, and transported in coolers at 4 °C. The sampling point coordinates have been determined using a global geographic positioning system (GPS GARMIN Olathe KS, US) (Fig. 2).

2.3 Sample analysis

Water physicochemical parameters such as electrical conductivity (EC), TDS (Total Dissolved Solids), pH and temperature were measured in situ using a Consort C535 multiparameter with specific probes, which had been pre-calibrated in the laboratory. Also, the dosage of the other parameters was conducted at Constantine University, Algeria, in the hydrochemical laboratory (Tab. 1).

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

Multivariate statistical analysis of the data was one of the methods used to analyze geochemical data, allowing to reduce the large dataset of variables to a few factors to elucidate correlations between chemical parameters. Our 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.

3 Resultants and Discussion

3.1 General hydrochemical features

3.1.1 Spatial distribution of groundwater salinity

The results of the groundwater physicochemical analysis are given in Tab. 2. Salinity is one of the most important water-classification parameters, Where our water's salinity values (TDS) range from 568 to 1586 $mg.l^{-1}$, and with an average of 906.3 $mg.l^{-1}$, this suggests low to medium mineralization of water during the dries season. While the TDS values in the wet season ranged from 1250 to 3270 $mg.l^{-1}$ with an average of 1822.16 $mg.l^{-1}$, our waters raise from medium to high mineralization. After the wet season we notice the significant increase in the salt charge, it suggests that the rainwater that feeds the groundwater influences the mineralization of our waters. While the pH values of the majority of the points are close to neutrality where they are between 6.5 and 7 and an average of 6.9 during the wet period, while the values oscillate between 6.5 and 7.21 and an average of 6.91 during the dry period, this indicates a slight seasonal variation.

Table 2 Descriptive statistics of Remila water parameters ($mg.l^{-1}$)

	Campaign	Mean	Median	Minimum	Maximum	Std.Dev.	Coef.Var.	Skewness	Kurtosis
pH	Dry period	6.87	6.92	6.52	7.02	0.13	1.90	-1.51	1.33
	Wet period	6.91	6.92	6.50	7.21	0.11	1.55	-1.27	7.09
TDS	Dry period	896.29	824.50	568.00	1586.00	254.52	28.40	1.29	1.13
	Wet period	1797.14	1710.00	1250.00	3270.00	485.57	27.02	1.67	2.87
Ca^{2+}	Dry period	134.74	132.26	40.08	252.50	39.36	29.21	0.49	2.41
	Wet period	132.14	128.26	44.09	248.50	46.42	35.13	0.76	1.18
Mg^{2+}	Dry period	50.83	35.88	6.96	239.64	53.54	105.34	2.63	6.50
	Wet period	56.83	52.68	28.80	129.48	22.48	39.55	2.04	4.59
Na^{+}	Dry period	55.56	41.75	11.96	145.59	34.78	62.61	1.45	1.49
	Wet period	69.46	62.11	29.67	162.15	33.45	48.16	0.93	0.41
K^{+}	Dry period	1.09	0.17	0.02	9.98	2.09	191.45	2.94	9.57
	Wet period	1.16	1.00	0.09	3.95	0.80	69.13	1.87	4.43
HCO_3^{-}	Dry period	174.75	164.70	54.90	280.60	53.64	30.70	0.31	-0.30

	Wet period	253.20	256.20	183.00	402.60	48.86	19.30	0.96	1.39
Cl^-	Dry period	122.80	118.93	35.50	312.40	58.36	47.53	1.16	2.07
	Wet period	125.79	117.15	35.50	333.70	83.41	66.31	1.22	0.90
SO_4^{2-}	Dry period	344.24	320.00	160.00	704.00	129.92	37.74	1.64	2.84
	Wet period	293.86	270.00	140.00	1250.00	188.44	64.13	4.05	20.20
NO_3^-	Dry period	-	-	-	-	-	-	-	-
	Wet period	8.19	3.60	0.20	39.00	11.09	135.45	1.96	2.42

Std.Dev: Standard Deviation; Coef.Var: Coefficient of variation.

The results of 35 points have led to generating a spatial distribution map of salinity (TDS) (Fig. 2). We note that the piezometric map of groundwater presents a rather close resemblance, reflecting changes in the mineralization of the water, upstream to downstream (south to north), although some specific trends are also apparent. This spatial variation is classifiable into two water types: the waters of the southern and western parts of the plain are low salty and the waters of the northern part near the Sabkha are moderately salty. This is possibly due to the massive influence of Sabkha's salt waters.

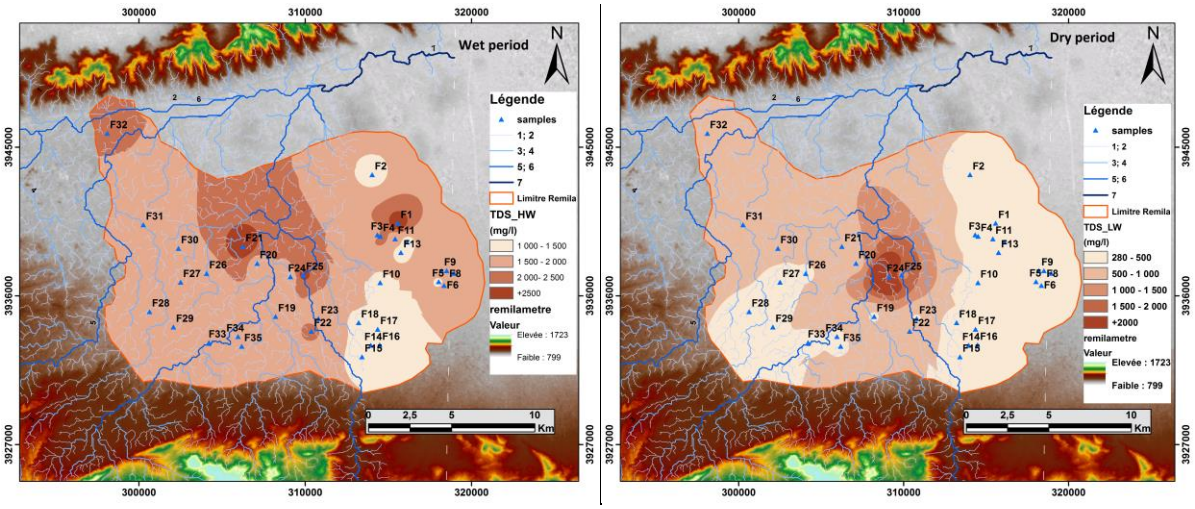

Fig. 2. Spatial salinity distribution map (TDS) of groundwater Remila (Khenchela)

3.1.1 Hydrochemical facies

Identifying the hydrochemical type of water is a useful tool for assessing water chemistry and processes such as mixing, cation exchange, and dissolution that affect the composition of groundwater. The Piper diagram [PIPER 1944] is considered to be the common method of performing multiple analyzes on the same graph. It allows for grouping samples and defining the various groundwater origins [WALTON 1965]. The main ionic species obtained from the geochemical analysis of 70 samples are projected on the piper diagram using DIAGRAMS 5.1 software [SIMLER 2012] (Fig. 3). On the bases of the results, we will deduce the dominance of three chemical facies in our waters, and this in the two companions (dry period

and wet period) : SO_4-Cl-Ca saltwater presented by certain points in the north-eastern part of the area near Sabkha, SO_4-Cl-Ca-Mg moderately saline waters presented by the majority of points and the good quality type HCO_3-Ca-Mg presented by some points in the southeastern part of the area.

Most of the water points show a tendency for SO_4^{2-} dominance in the anionic triangle, especially samples taken after the wet season, while in the cationic triangle there is a tendency towards Ca^{2+} domination. This suggests that the aquifer is affected by different hydrochemical processes: ionic exchange with the substratum, leaching and dissolution of sediments in the southern part (Recharge areas after a wet season) and saltwater intrusion of the Sabkha waters in the northeastern regions.

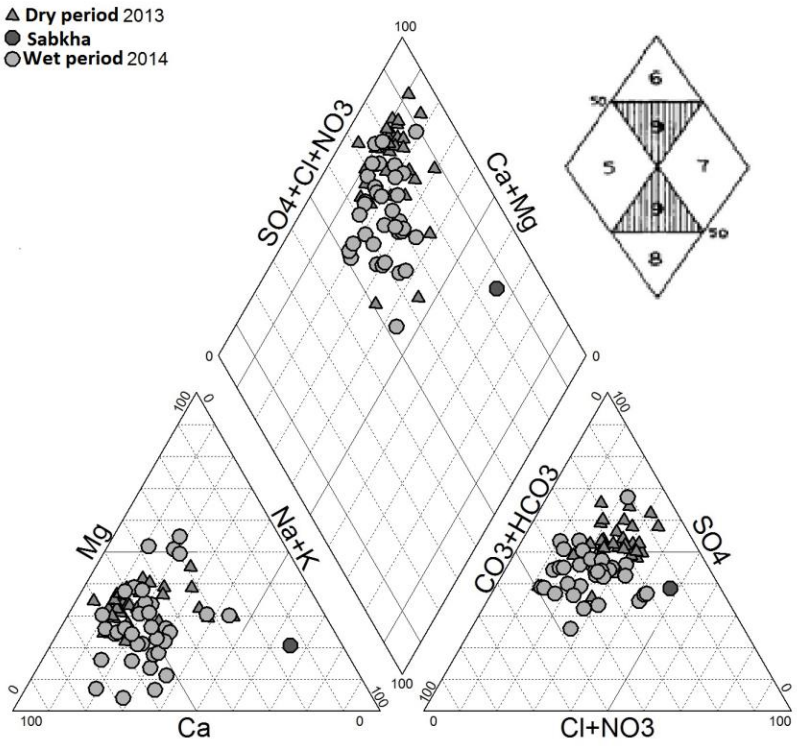

Fig. 3. Piper diagram of Remila groundwater (Dry period and Wet period).

3.2 Statistical Analysis

Descriptive statistical evaluation of data is a critical step in any statistical analysis (Tab. 2) [YANG *et al.* 2011; HOSSEINI *et al.* 2014]. The measured parameter values are characterized by very high variance. The most important factor that can describe the variability of the water parameter values is the variance coefficient (VC). A low variance coefficient (<10 %) for pH was calculated suggesting a low spatial variability in the study area. While for the TDS, HCO_3^-, Ca^{2+}, and Fe^{2+}, a moderate coefficient of variance (20-50 %)

was observed, indicates moderate spatial variability for these parameters, and is mainly influenced by natural factors. Nonetheless, for Mg^{2+}, Na^{+}, K^{+}, SO_4^{2-}, Cl^{-} and NO_3^{-}, very high CV values exceeding 50% were observed, suggesting a very high spatial variability and these parameters are affected by natural and anthropogenic factors.

The Skewness reflects the symmetric distribution when these values are under 0 the totality of the data is below the average. For the data to have a normal distribution, the skewness value equals zero [GALVAO *et al.* 2013; BROVELLI *et al.* 2011]. The calculated skewness values of Ca^{2+}, Na^{+}, and HCO_3^{-} are close to zero indicate that the data follow a normal distribution. However, other parameters have values >1, this does not require a data transformation. OLIVER *et al.* [2002], KERRY and OLIVIER [2007] and OLIVER [2010] have shown that Skewnees values outside the ±1 standard limits envelope do not necessarily imply the need to transform the data into statistics for further study, especially when the data values were high.

3.2.1 Pearson's correlation matrix

Many significant correlations between the different ions were established using the correlation matrix of the various parameters (Table 3). A strong correlation (r> 0.7) was found between the chemical tracers SO_4^{2-}, Cl^{-}, Mg^{2+}, Na^{+}, Ca^{2+}, Sr^{2+} and total dissolved solids (TDS), indicating an evaporite origin (from NaCl, $CaSO_4$, $CaSO_4$ $2H_2O$, $MgSO_4$ or $SrSO_4$) of these elements in the water. However, this is not the case for HCO_3^{-} which has a low correlation with the salinity indicator TDS, which is explained by its low concentration in the water solution that ranges between 54.9 to 280.6 mg.l-1. Besides, the correlation coefficients between chloride (r = 0.81) and sodium (r =0.81), with the (TDS), suggests the same origin for these two elements. On the other side, there is a slight difference between sulfate (r=0.95), magnesium (r=0.87) and calcium (r=0.66) correlation coefficients with TDS, Can be explained by the unconservative transport of calcium and magnesium ions (cation exchange with clay minerals which are most abundant in the area and/or participate in precipitation/dissolution reactions) [VAN BREUKELEN *et al.* 1998].

Concerning the relationship between anions and cations, significant correlations were found between Cl^{-} and Na^{+} (r=0.55), 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 comes from the dissolution of 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 can be explained by 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 Cl^{-} with Mg^{2+} (0.68). This is due to the water

salinity that is caused by several processes that characterize the highly mineralized waters, including an exchange of cations and dissolution of gypsum and halite that can increase the concentrations of calcium, magnesium, and chloride, respectively.

Table 3. Correlation matrix of different groundwater parameters ($mg.l^{-1}$)

Variable	pH	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	Fe	Mn	Sr
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

We carried out the main component analysis (PCA) and hierarchical clustering analysis (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.

3.2.2 Principal component analysis (PCA)

More and more studies are based on statistical analysis to define water types; one of the most recommended approaches is the principal component analysis [FARNHAM *et al.* 2003 in OLIVIER 2015; AYADI *et al.* 2018]. In the Remila aquifer samples, the variable factors F1-F2 (Fig. 4(a)) (Table 4) show that this plan 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+} and therefore has a mineralization axis of evaporites and salinity. A very good correlation exists between TDS, SO_4^{2-} and Mg^{2+}. The F2 explains 17.21% of the total variance, which is positively associated with pH and HCO_3^-, suggesting that the dissolution of carbonates does not contribute to the mineralization of water.

The projection results variables and individuals in the factorial plan (F1, F2) shown in Fig. 4(a), allow nodes identifies three different water groups. The first type (I) are saline waters

presents with (23%), where TDS exceeds 1000 mg.l-1 and which are characterized by a high concentration of SO_4^{2-}, Type (II) are non-saline water presents (51%) waters with high concentrations of HCO_3^- and Type (III) is moderately saline waters with mixed facies presents in the eastern part of the region with (26%).

Table 4. Varimax factor loading matrix, communalities for each variable analyzed

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	-0.2245	-0.5564	0.4408	0.1886	-0.2360
TDS	-0.9795	0.0831	0.0054	-0.0857	0.0711
Ca	-0.6711	-0.3059	-0.4608	0.0097	-0.2072
Mg	-0.8954	-0.0599	0.2170	0.0042	0.0861
Na	-0.7563	0.3892	0.3325	-0.1522	0.2471
K	-0.8628	0.1267	0.1683	-0.0418	0.0688
HCO_3	-0.0889	0.8501	-0.0524	-0.0639	0.2252
Cl	-0.8338	-0.3110	-0.0842	-0.0693	-0.0157
SO_4	-0.9552	-0.0205	0.0742	-0.0525	0.0339
Fe	-0.2704	0.0499	-0.5723	0.5659	0.1012
Mn	0.2749	0.4881	0.4029	0.2935	-0.3649
Sr	-0.7282	0.3298	-0.3126	0.1030	-0.1388

3.2.3 Hierarchical cluster analysis (HCA)

The ascending hierarchical clustering (AHC) is a powerful multivariate statistical technique to analyze water chemistry data for geochemical model formulation [YIDANA 2008; AHOUSSI *et al.* 2011].

The results from the analysis of the hierarchical ascending data classification can be observed in the dendrogram using the Euclidean distance for similarity measures (Fig. 4(b)), highlights three principal groupings of the variables. The first group includes the individus (waters points): he first group is that of waters occupying the north-western part of the area, are salty waters characterized by a dominance of SO4, the second group that presents the majority of waters in the eastern and south-eastern part of the region, characterized by low salinity with a mixed face, in the last group, the waters of the south-western part are moderately saline with a dominance of HCO_3.

The results provided by the PCA of the individual samples and ascending hierarchical clustering are in the perfect agreement since they demonstrated that water mineralization is

dominated by sulfate. Besides, the typology of the water samples can be represented by three facies.

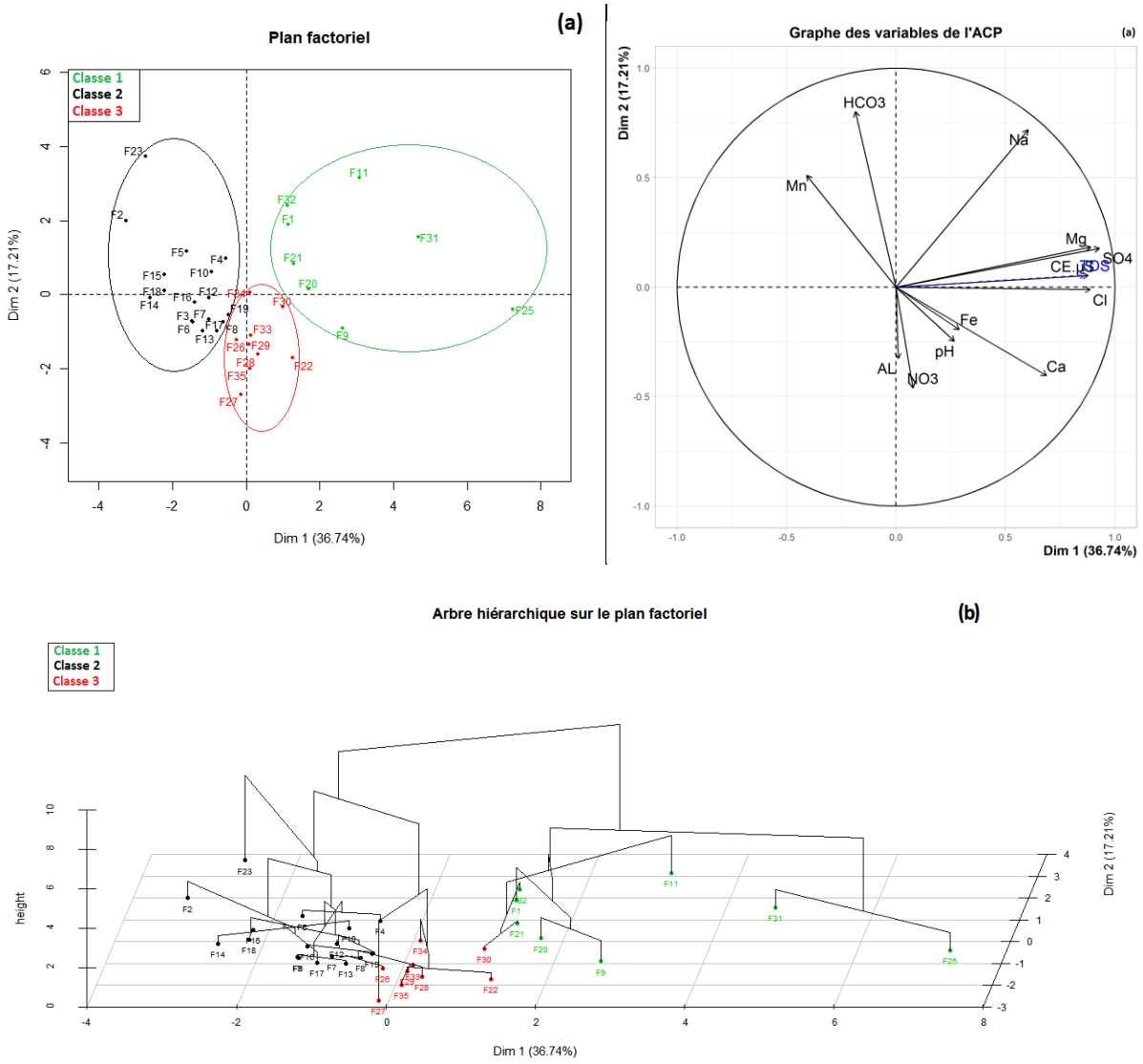

Fig. 4. Statistic analysis; (a) Principal component analysis, (b) the Ascending hierarchical clustering of Remila waters (Khenchela)

3.3 Groundwater mineralization processes

Correlations show a statistical relationship between two variables or more. Our results confirm a significant correlation between SO_4^{2-}, Mg^{2+}, Cl^-, Ca^{2+}, Na^+, HCO_3^-, Sr^{2+}, K^+, and TDS, indicate the contribution of these elements to the salinity of the groundwater and suggest that a common source of mineralization may be the dissolution of the evaporitic rocks. Such results require geochemical calculations of speciation-solubility in order to identify the dominant processes, which influence the Remila plain groundwater hydrogeochemistry.

3.3.1 Water-rock interaction

To assess the water-rock interaction processes, diagrams ion ratio of Ca^{2+}/Na^{+} versus HCO_3^{-}/Na^{+} and Ca^{2+}/Na^{+} versus Mg^{2+}/Na^{+} were used to identify the influence of silicate weathering, dissolution evaporites and carbonate alteration on mineralization of groundwater in the study area. The projection results of the water points (Fig. 5(a)), infer that the bulk of the waters are affected by silicate weathering with a bent towards carbonate dissolution, especially after the wet period. The spatial distribution suggests that the waters near the limestone formations of the eastern part are more or less influenced by carbonate dissolution, whereas the waters of the northwestern part are affected by silicate alteration. The normalization of Na by intake Ca versus Mg (Fig. 5(b)), indicates that the bulk of Mg within the waters of the Eastern part is released by carbonate dissolution, in contrast, the Mg within the waters of the western part are influenced by silicate weathering. The Ca^{2+}/Mg^{2+} ionic ratio is widely used to identify the dissolution of calcite and dolomite, when the ratio values are ≤1 indicates the dominance of the dissolution of dolomite, if the values are between 1 and 2 indicates the dominance the dissolution of calcite and cons if the values are ≥2 waters are affected by silicate minerals [SRINIVASAMOORTHY *et al.* 2014; SINGH *et al.* 2017]. The ratio calculation outcomes suggest that, the waters in the extreme south are dominated by means of dolomite dissolution, the majority of the waters in the primary central part of the area are dominated by calcite dissolution, whilst the northern part is affected with silicate weathering.

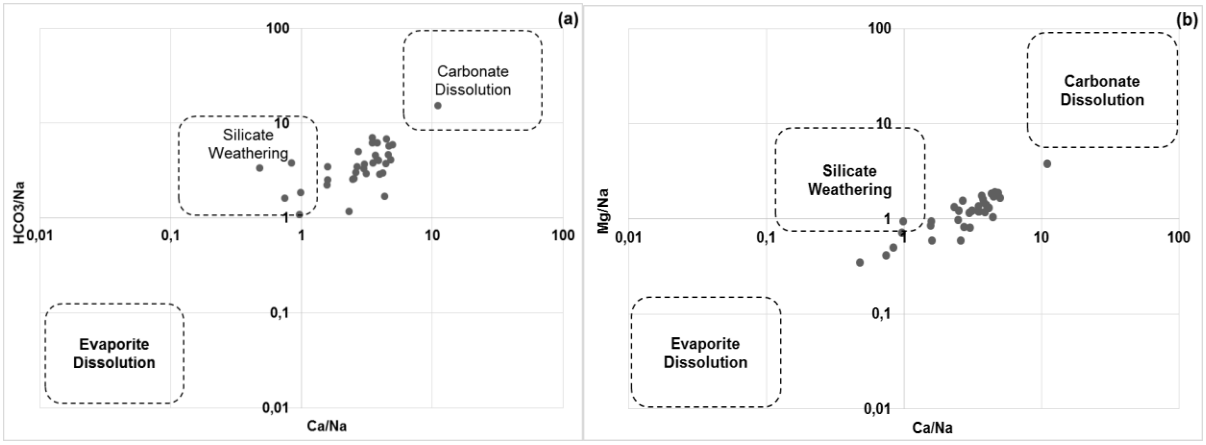

Fig. 5. Scatter plots of a) Ca^{2+}/Na^{+} versus HCO_3^{-}/Na^{+}, b) Ca^{2+}/Na^{+} versus Mg^{2+}/Na^{+} ration of the Remila groundwater samples

The Gibbs diagrams (GIBBS 1970) are widely used to assess the functional source of ions dissolved in water such as; dominance of precipitation, weathering of rocks and dominance of evaporation which controls the water chemistry (SINGH *et al.* 2011; VAROL and DAVRAZ 2014; MASOUD *et al.* 2018). The chemical data are plotted in a semi-logarithmic dispersion

of TDS values versus anion ($Cl^-/(Cl^-+HCO_3^-)$) and cations ($Na^+/(Ca^{2+}+Na^+)$) ratios, where all concentrations Ionic values are expressed in $meq.l^{-1}$ (Fig. 6 (a, b)).

As shown by the data projected in the Gibbs diagrams, the majority 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. The mineralization of our waters is therefore controlled by the dissolution of evaporitic rocks and is also affected by the waters of Sabkha, which are exposed to intense evaporation with chemical precipitation of minerals, which increases the salinization of our waters, particularly in the northeastern part of the area.

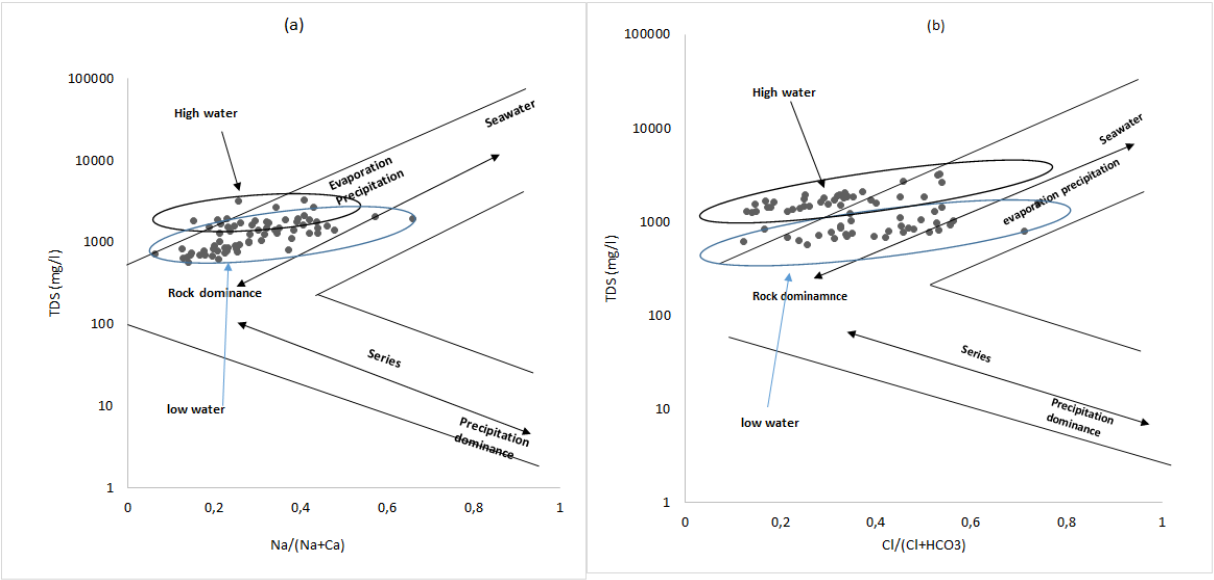

Fig. 6. Gibbs diagrams of Remila groundwater

Another index is commonly used to identify water-rock interactions, as well as hydrochemical processes affecting groundwater chemistry [PLUMMER *et al.* 1976; DAVID *et al.* 1999; KUMARI *et al.* 2013; AYADI *et al.* 2018]. The saturation index (SI) describes the level of saturation of the water towards the various minerals; when SI = 0, the minerals in the aqueous solution are in equilibrium; when SI <0, the minerals of the aqueous solution are under saturated which contribute to the dissolution of the minerals, while SI> 0 indicates a saturation of solution will contribute to the precipitation of the minerals [APPELO and POSTMA 1994]. The mineral saturation index was calculated using the PHREEQC geochemical modeling program, using the following equation (GARRELS and MACKENZIE 1967):

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

SI: Saturation Index

IAP: Ion activity product

K_t: The equilibrium solubility constant

Results showing that the area's groundwater is under-saturated with respect to gypsum, anhydrite, and dolomite (SI < 0) indicate that these minerals should be dissolved in our water. While groundwater is slightly under-saturated with calcite and aragonite, this means it has some equilibrium with these minerals, but these minerals may have influenced the chemical composition of the water (Fig. 7).

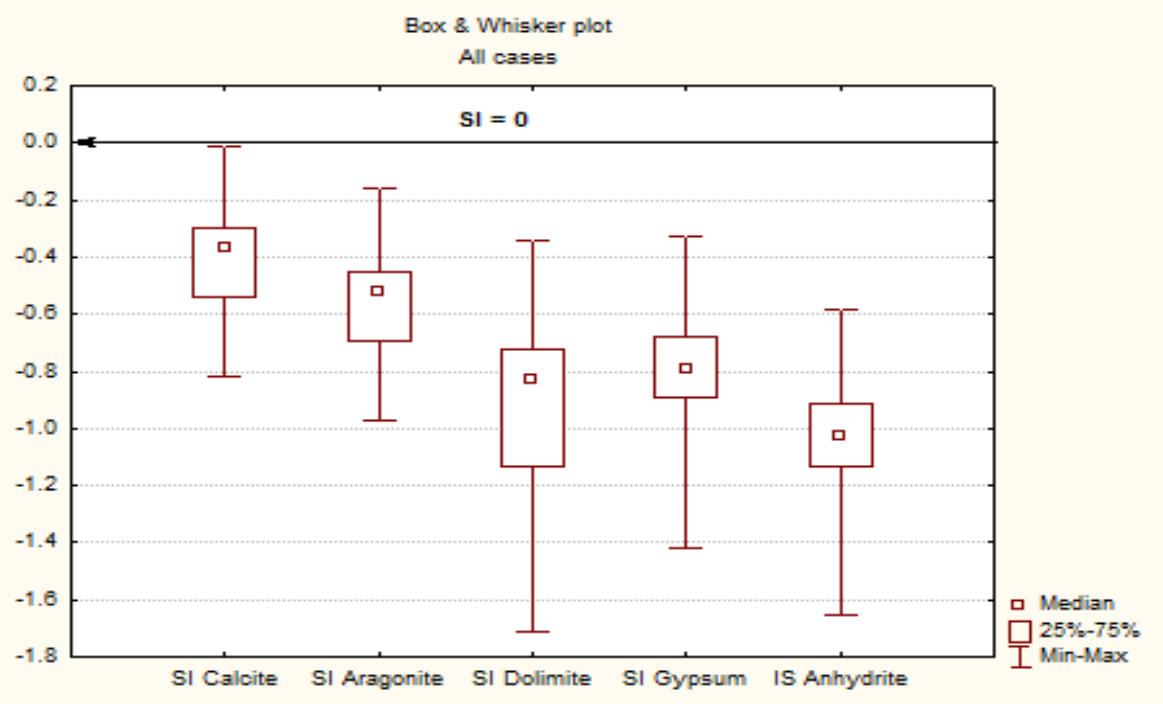

Fig. 7. Saturation index (SI) variability diagrams in groundwater at Remila (Khenchela)

3.3.2 Cationic exchange

Most of the results show an excess concentration of cations by anion supply, which indicates that another source of these cations should be possible, such as exchange. Nevertheless, SCHOELLER'S [1965] proposed chloroalkaline index (CAI) can be used to determine the degree of ion exchange reactions between the aquifer substratum and groundwater. It is a commonly used tool for recognition of dominant processes of ion exchange in groundwater [AYADI *et al.* 2018; ABU-ALNAEEM *et al.* 2018]. The CAI is calculated using the equation $(Cl^-(Na^+ + K^+))/Cl^-$ where the values are in meq.l^{-1}. If the CAI values tend to decrease (negative), 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. Thus, 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. While if the CAI values are close to zero show a balance, this implies the absence of an exchange process.

The calculated chloro-alkaline index in the study area shows positive values for most groundwater samples (68%), which 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 26% of the samples have values close to zero, which imply an equilibrium, indicates an absence of ion exchange, they are 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 are found in the northeastern part of the region.

Wide fluctuations in the concentration of major ions occur by various processes, ion exchange often causes changes or reversals of groundwater cationic concentrations. Studying the relationship between (Ca^{2+}+Mg^{2+}) and (HCO_3^{-}+SO_4^{2-}) will however allow us to identify the processes that influence groundwater mineralization. The binary diagram of (Ca^{2+}+ Mg^{2+}) versus (HCO_3^{-} + SO_4^{2-}) (Fig. 8 (a)) shows a projection of the water points around the line (1:1). Generally, the water points, which are close or on the line (1:1), are under the influence of the dissolution of calcite, dolomite, anhydrite, and gypsum [HAMZAOUI-AZAZA *et al.* 2012; HASSEN et al. 2016]. While the water points that exist above the line (1:1), present an excess of (Ca^{2+}+Mg^{2+}) that are accompanied by ion exchange [TLILI-ZRELLI *et al.* 2013]. On the other hand, the water points located below the line (1:1), have a deficit in (Ca^{2+}+Mg^{2+}); this decrease in concentration is due to reverse ion exchange [RINA *et al.* 2013]. The result of the water points projection in the diagram (Fig. 8(a)) shows that most waters are above line (1:1) due to excess (Ca^{2+}+Mg^{2+}) and this indicates that reverse ion exchange is a very abundant geochemical process in the region. The water points located in the northeastern part near Sabkha (saltwater) are projected below the line (1:1), suggesting a deficit in (Ca^{2+}+Mg^{2+}), which indicates that the waters in this part of the study area are under the influence of ion exchange and saline intrusion.

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 [BEKKOUSSA *et al.* 2013; KRAIEM 2015]. The diagram (Ca^{2+}+Mg^{2+})-(HCO_3^{-} +SO_4^{2-}) versus (Na^{+}+K^{+})-Cl^{-} in ($meq.l^{-1}$) (Fig. 8(b)) 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. Sample distribution indicates that the most saline groundwater in

the western part of the area has migrated in a direction that is characterized by a rise in Ca^{2+} and Mg^{2+} and a decrease in Na^{+} and K^{+} concentrations, which suggests that the water mineralization is affected by rock dissolution accompanied by ion exchange. Although water points located in the northeast of the area are characterized 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, and this is favored by the saline intrusion of Sabkha waters [APPELO 1994]. These results confirm that two main processes control our water hydrochemistry: the dissolution of evaporitic rocks, and ion exchange.

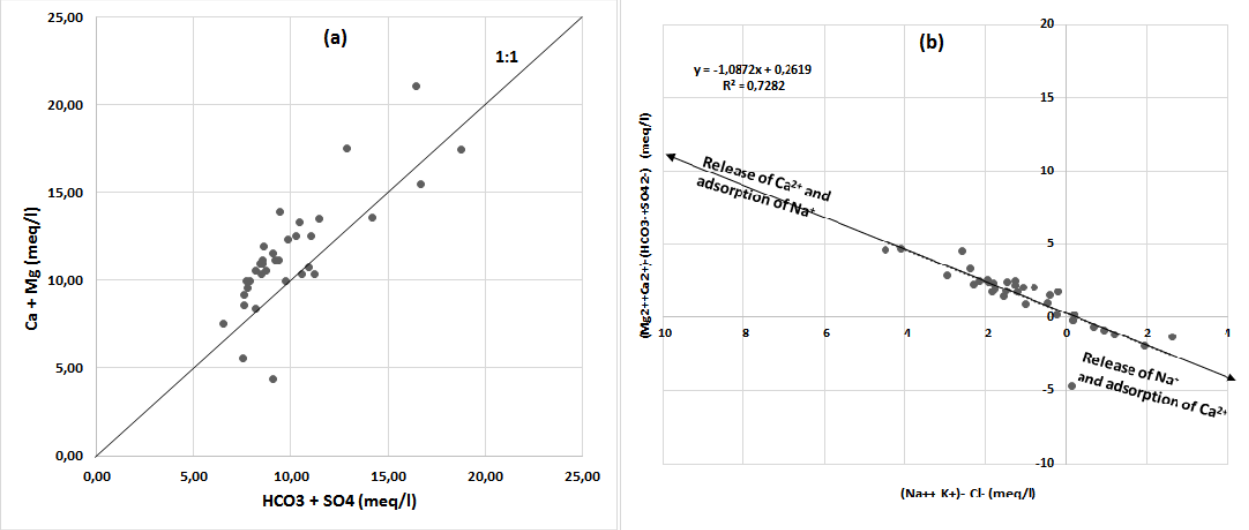

Fig. 8 Scatter plots of a) $(Ca^{2+}+Mg^{2+})$ versus $(HCO_3^{-} + SO_4^{2-})$ b) $(Ca^{2+}+Mg^{2+})$-$(HCO_3^{-}+SO_4^{2-})$ versus $(Na^{+}+K^{+})$-Cl^{-} in $(meq.l^{-1})$ of the Remila groundwater simples

4 Conclusion

Salinization of water is considered a major problem of land degradation in arid and semi-arid regions. Our research focuses on the endorheic basin of Remila (Khenchela), which is characterized by a semi-arid climate with low and sporadic rainfall. In the study area, the principal source of drinking and irrigation water is groundwater (Plio-quaternary aquifer). A hydrogeochemical and statistical approach was applied in the context of identifying the various salinization processes and the origin of degradation of the aquifer system in the study area.

The results indicate the predominance of three groundwater facies; SO_4-Cl-Ca-Ca salt water located to the northeast of the area, SO_4-Cl-Ca-Mg moderately saline water which presents the majority of water points, and the type of good quality HCO_3-Ca-Mg found in the south-

eastern part of the area. The statistical analysis of the measured parameters reveals a normal distribution of the data, and the VC indicates a moderate to high spatial variability, and this suggests that the parameters measured are mainly affected by environmental factors and more or less by anthropogenic activities. As well as significant correlations (r>0.7) between the elements SO_4^{2-}, Cl^-, Mg^{2+}, Na^+, Ca^{2+}, Sr^{2+} and the global salinity of water (TDS) were found, suggesting a common origin of evaporite dissolution. Three water groups were successfully identified using PCA and HCA through multivariate statistical analysis; 1) Saltwater (23%), where the TDS> 1000 mg.l-1 with a high concentration of SO_4^{2-}, 2) Moderately saline waters also present (51%) but with high concentrations of HCO_3^-, 3) The bulk of the waters are moderately saline (26%) but with a mixed facies.

The use of ionic ratios with various binary diagrams further suggests that the geochemical processes controlling the Remila aquifer system are; Evaporite dissolution and/or precipitation (calcite, gypsum, halite, and dolomite) shall be accompanied by ionic exchange and/or reverse ionic exchange. In the northeastern part of the Sabkha is produced as well as a saline intrusion of waters, which was favored by intense farmers ' exploitation of the aquifer.

The results of this work can be used as a conceptual platform for future research, and to prepare a sustainable development plan in the region take into account the risks caused by human activity. For example, groundwater overexploitation can be managed by installing a suitable and economical irrigation system with the planting of drought-tolerant species with the incorporation of unconventional water into the irrigation system.

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Conflict of interest

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Tables:

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

Table 2. Descriptive statistics of Remila water parameters (mg/l)

	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

Std.Dev: Standard Deviation; Coef.Var: Coefficient of variation.

Table 3. Correlation matrix of different water parameters in the Remila plain (Khenchela) (mg/l)

Variable	pH	TDS	Ca	Mg	Na	K	HCO_3	Cl	SO_4	Fe	Mn	Sr
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

Table 4. Varimax factor loading matrix, communalities for each variable analyzed

Parameters	Factor 1	Factor 2	Factor 3	Factor 4	Factor 5
pH	-0.2245	-0.5564	0.4408	0.1886	-0.2360
TDS	-0.9795	0.0831	0.0054	-0.0857	0.0711
Ca	-0.6711	-0.3059	-0.4608	0.0097	-0.2072
Mg	-0.8954	-0.0599	0.2170	0.0042	0.0861
Na	-0.7563	0.3892	0.3325	-0.1522	0.2471
K	-0.8628	0.1267	0.1683	-0.0418	0.0688
HCO_3	-0.0889	0.8501	-0.0524	-0.0639	0.2252
Cl	-0.8338	-0.3110	-0.0842	-0.0693	-0.0157
SO_4	-0.9552	-0.0205	0.0742	-0.0525	0.0339
Fe	-0.2704	0.0499	-0.5723	0.5659	0.1012
Mn	0.2749	0.4881	0.4029	0.2935	-0.3649
Sr	-0.7282	0.3298	-0.3126	0.1030	-0.1388

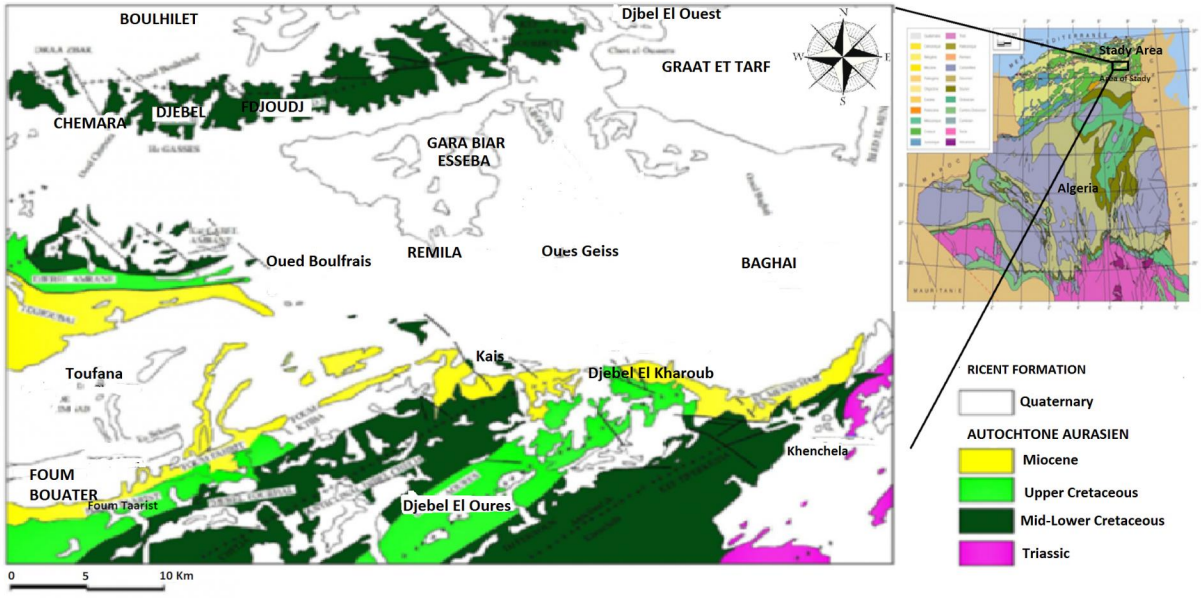

Fig. 1. Map showing location and geological formations of the study area

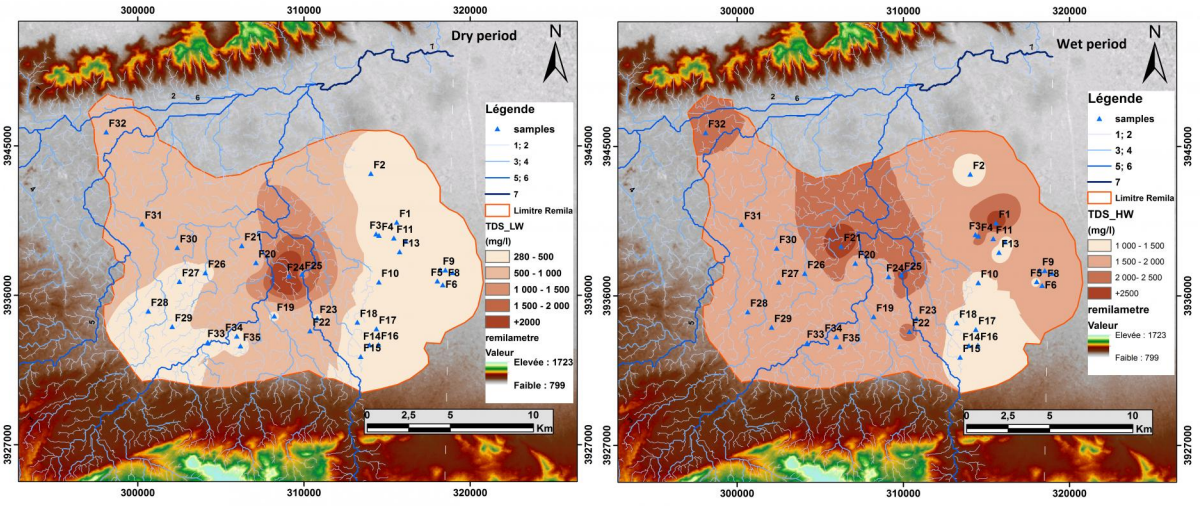

Fig. 2. Spatial salinity distribution map (TDS) of groundwater Remila (Khenchela)

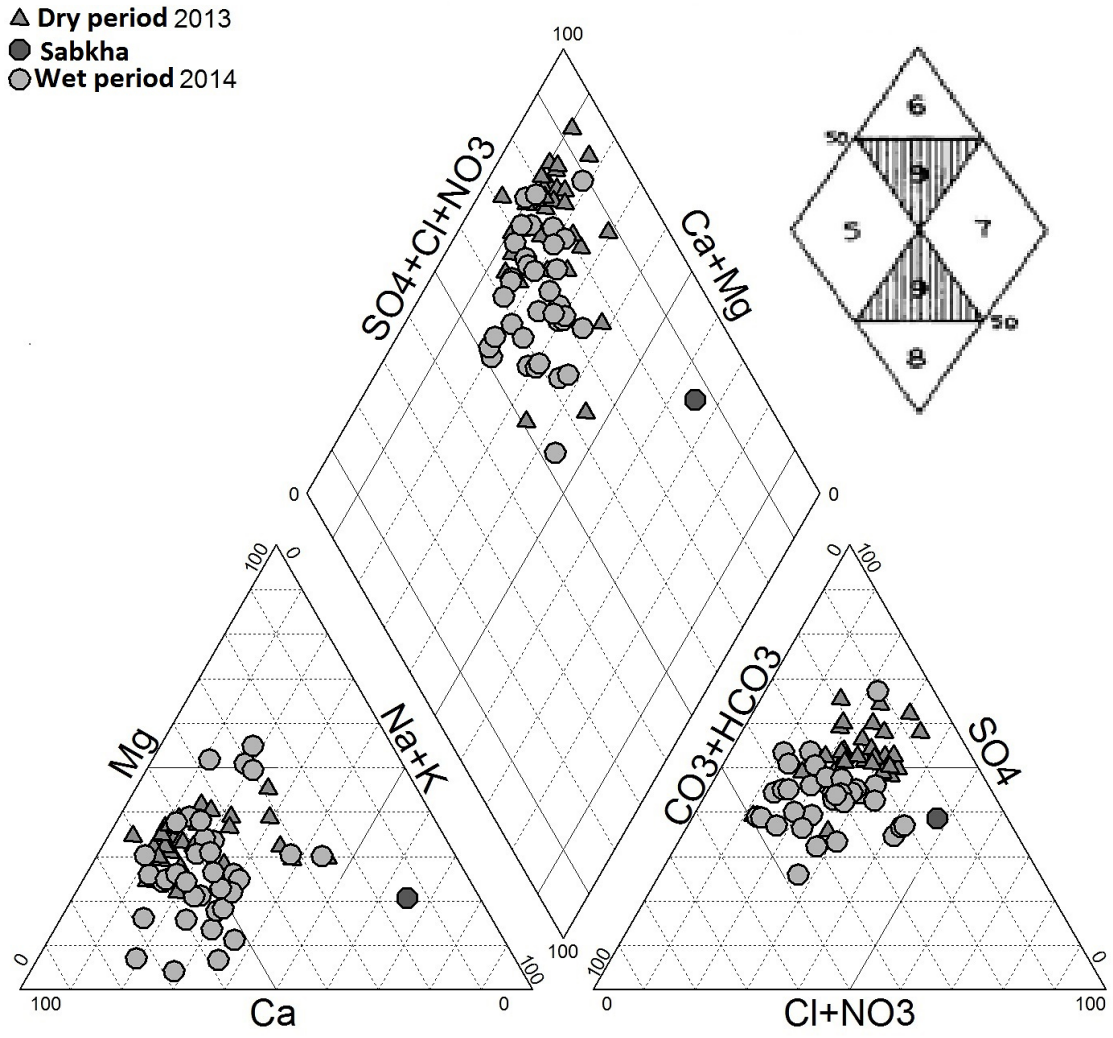

Fig. 3. Piper diagram of Remila groundwater (Dry period and Wet period).

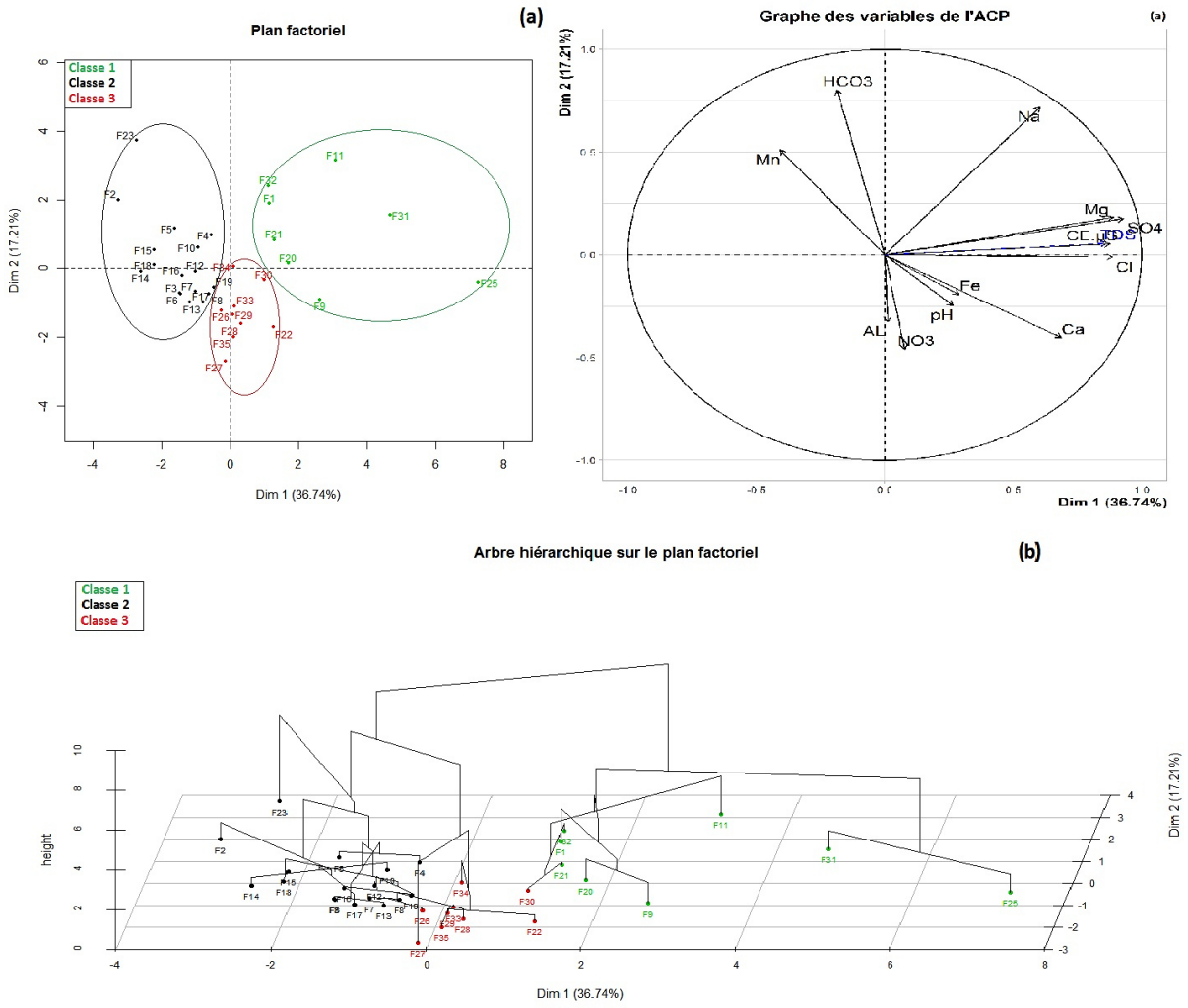

Fig. 4. Statistic analysis; (a) Principal component analysis, (b) the Ascending hierarchical clustering of Remila waters (Khenchela)

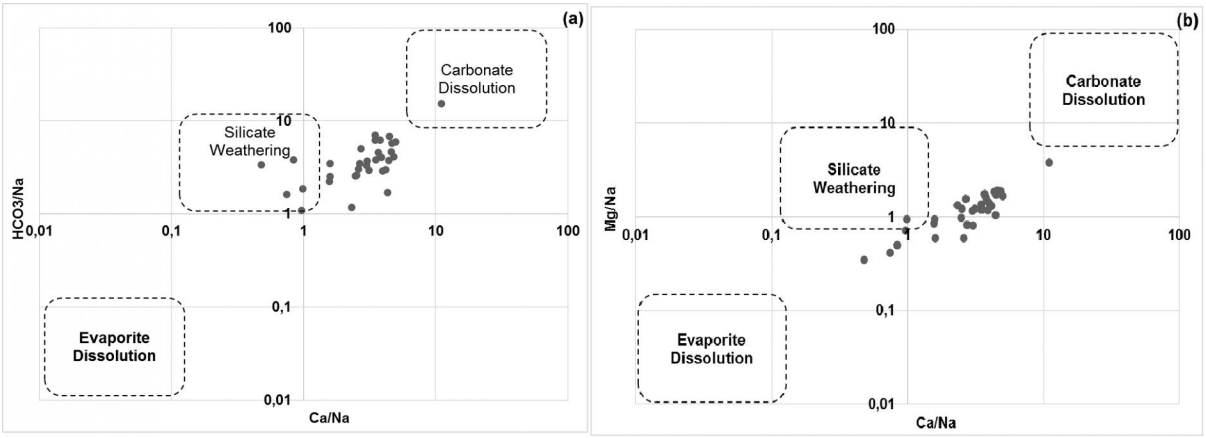

Fig. 5. Scatter plots of a) Ca2+/Na+ versus HCO3-/Na+, b) Ca2+/Na+ versus Mg2+/Na+ ration of the Remila groundwater samples

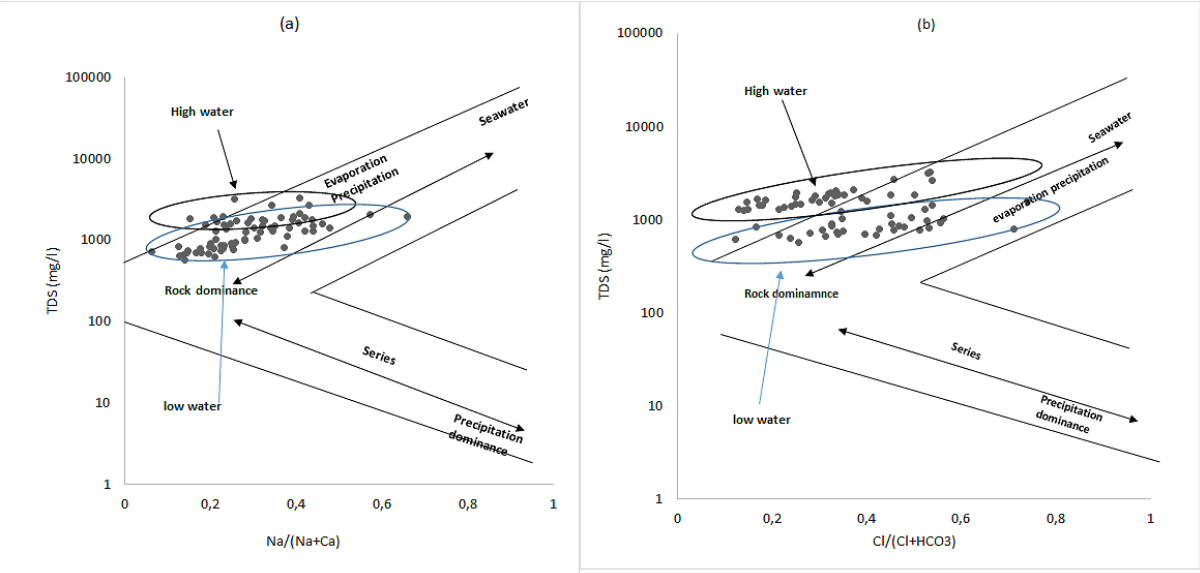

Fig. 6. Gibbs diagrams of Remila groundwater

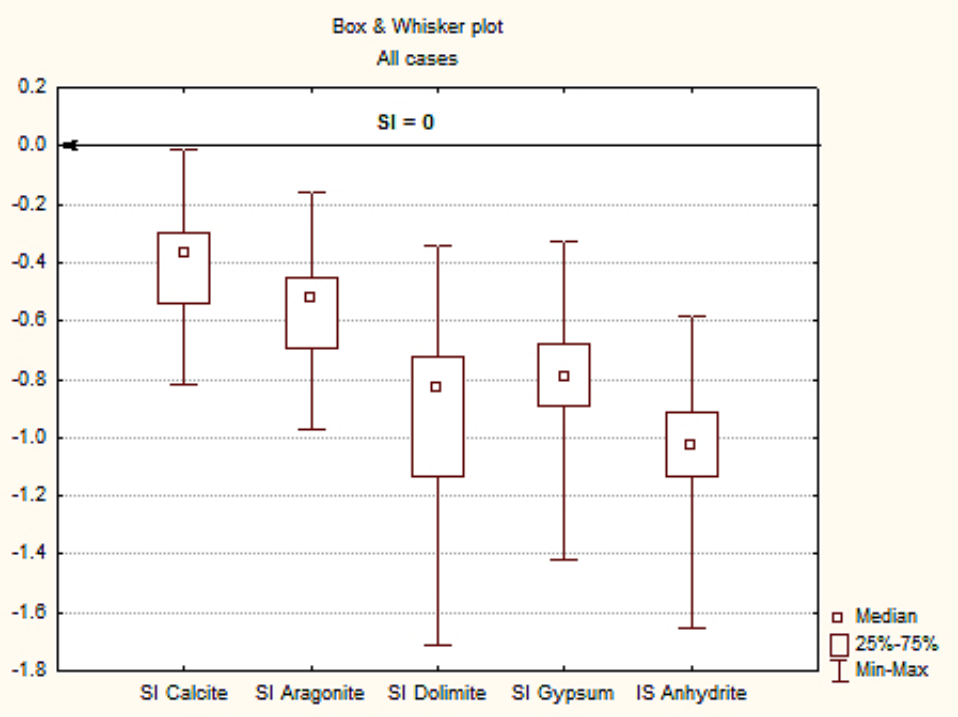

Fig. 7. Saturation index (SI) variability diagrams in groundwater at Remila (Khenchela)

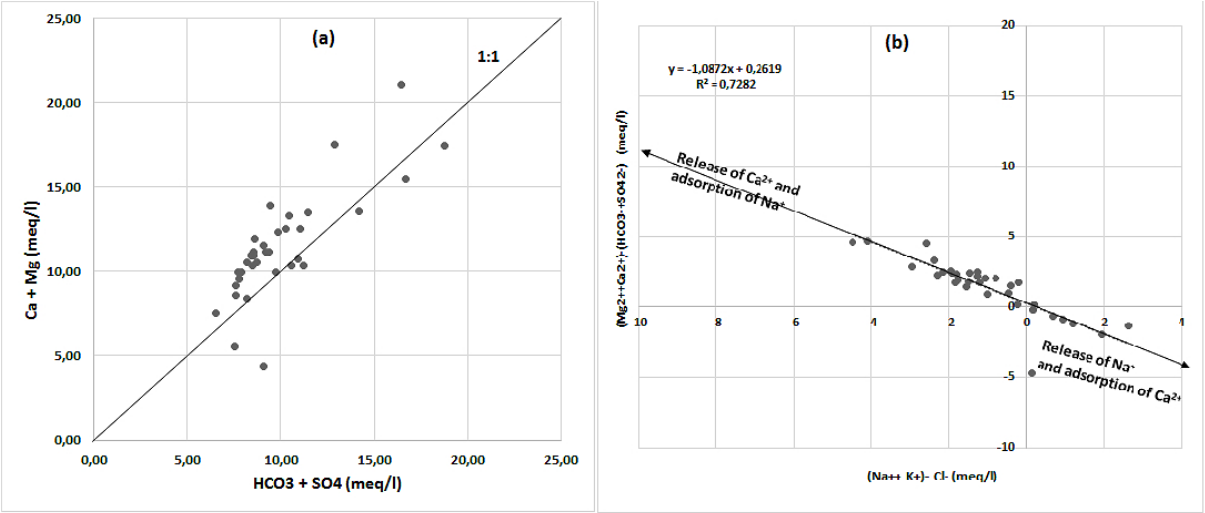

Fig. 8. Scatter plots of a) (Ca2++Mg2+) versus (HCO3- + SO42-) b) (Ca2++Mg2+)-(HCO3-+SO42-) versus (Na++K+)-Cl- in (meq/l) of the Remila groundwater simples

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Fig. 1. Map showing location and geological formations of the study area

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