Geochemical Assessment of Environmental Impact on Groundwater Quality in Coastal Arid Area, South Eastern Tunisia

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Abstract: Groundwater contamination has been recognized as one of the most serious problems in semi-arid and arid area (e.g. Zarzis aquifer, south-eastern Tunisia). The groundwater chemistry evolves rapidly and the salinity goes up considerably. A geochemical survey was carried out in which 23 groundwater samples were collected. EC, pH, TDS and major ions were measured and analyzed. Geochemical modeling, Piper Diagram, Q-mode hierarchical cluster and PCA were used to assess groundwater mineralization processes. Spatial variability of the different groundwater parameters was examined using semivariogram analysis. Results revealed that the Na-Cl-Ca-SO_4-K is the dominant water type, suggesting rock-water interaction and dissolution of NaCl, $CaSO_4$, $2H_2O$ and KCl from sebkhas to be the main processes controlling groundwater mineralization in study area. Hierarchical Cluster Analysis (HCA) showed that groundwater is grouped in two clusters: the first, located in the southern part of the study area, is influenced by salt depressions in which a high potassium concentration was found. The second cluster characterized by rock-water interaction is located in the northern par of study area. Spatial development of groundwater flow and TDS were analyzed using variographic analysis and kriged maps were plotted. The method has succeeded in effectively extracting useful information, and improving the analysis of salinity and piezometric level, thereby playing an important role in qualitative and quantitative predictions. No reversal of the hydraulic gradient is detected in the study area, which eliminates any assumption on seawater intrusion in the region.

Keywords: Geochemistry, salinity, Statistics, geostatistics, arid area, Tunisia.

1. INTRODUCTION

Groundwater management, especially in arid and semi-arid areas, is very important to meet the increasing demand of water for domestic, agricultural and industrial uses. Various management measures require the spatial and temporal development of groundwater chemical composition [21]. In South-eastern Tunisia (e.g. Zarzis Peninsula), groundwater contamination has been recognized as one of the most serious problems. The groundwater chemistry evolves rapidly and the salinity goes up considerably. Several factors cause the increase in groundwater salinity. Some of these factors are local, such as hydrogeological conditions, rate of natural recharge and irrigation [23], while others are regional in nature, including the aridity of the environment and the irregular and unpredictable occurrence of rainfall.

Numerous studies undertaken worldwide dealt with groundwater quality in coastal areas. Geochemical assessment as used in mediterranean basin and in somewhere in the world. Hydrogeochemical and statistical analysis were used by Kharroubi *et al.* [19], in order to identify groundwater salinization origin in Jerba coastal aquifer southeast Tunisia. Lachaal *et al.* [22] used hydrodynamics and geochemistry to characterize a complex coastal aquifer of Zeramdine and Mahdia-Jebeniana in central Tunisia. Kouzana *et al.* [20] were used hydrochemical to assess seawater intrusion and associated processes in the Korba aquifer northern Tunisia. In the world, geochemichal modeling approach was widely used to assess groundwater quality and processes controlling groundwater chemistry [6, 10, 24, 29, 35, 37, 41].

Application of statistical methods such as Hierarchical Cluster Analysis (HCA), Principal Component Analysis (PCA) for interpretation of the hydrogeochemical data sets offers a better understanding of the hydrochemical processes involved in the characterization of a groundwater quality [2, 20, 38]. Associated with geostatistical analysis, these techniques permit identification of the possible processes responsible for the variations in groundwater quality [35,38], thereby offering valuable tools for developing appropriate strategies for effective management of the water resources [24, 29, 37]. Geostatistical interpolation provides the best linear unbiased prediction for spatially dependent properties [17]. Kriging has been frequently used for the spatial interpolation of groundwater geochemistry data [1, 3, 4].

A groundwater geochemical study consists of two particular stages. The first involves collecting and analyzing water samples. The second step concerns

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the treatment and interpretation of available numerical information by plotting the geochemical values on maps, and interpretation of the results. Groundwater sampling and measurement are generally carried out at spatially random locations in the field, while most of the groundwater models require these measurements within a pre-specified grid.

This study proposes to integrate geochemical modelling, statistical analysis (HCA, PCA) and kriging techniques to characterize the geochemistry of various categories of groundwater in order to identify the main processes that act on groundwater quality in Zarzis aquifer. Pincipal Component Analysis (PCA) and Kriging techniques allow to work in a reduced multi-variate space, and to establish their spatial distribution by the computation of variograms. Likewise, it is intended to produce maps of groundwater quality using kriging and cokriging techniques.

2. MATERIAL AND METHODS

2.1. Site Selection and Characteristics

The study area consists of Zarzis peninsula is located in southeastern Tunisia, within the eastern coastal Plain of Marine Jeffara (Figure **1**). Study area is

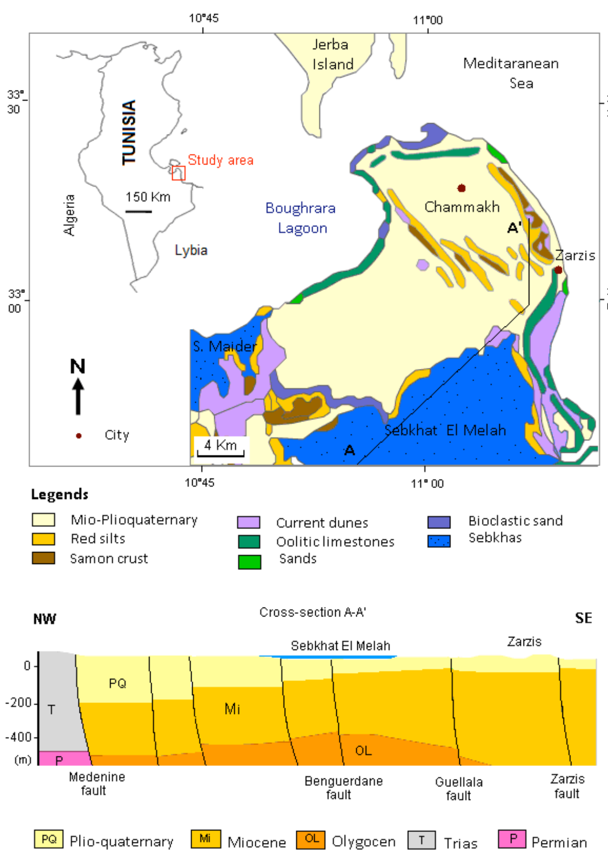

Figure 1: Location and geological map of study area (After [16,26]).

bounded to the south by Sebkhat El Melah, to the east and the north by Mediterranean Sea, to the west by Boughrara lagoon and sebkhat El Maider. It covers an area of almost 86700 ha between the longitudes 32°30' and 33°30'N the latitudes 10°45' and 11°30'E. The study area is very flat, with a poor hydrographical net-work. The Zarsis Peninsula is characterized by an arid to semi-arid climate influenced by hot dry air masses coming from the desert. Rainfall is variable and irregu-lar. The mean rainfall varies from 100 to 225 mm/year [42]. Humidity ranges from 43 to 84%. The average annual temperature ranges from 5.9 to 42.6 ° C with an average of 21 °C. August is the hottest month and February is the coldest. Evaporation is irregular both seasonal and monthly scale. It reaches a maximum rate of 254 mm/month during the summer. Evaporation rates exceed 1,700 mm / year [31].

2.2. Geological and Hydrogeological Settings

The geological settings consist of alternating continental and marine origin deposits. A marine, the oldest submerging layers is the superior Permian, and the most recent formations are of the recent Quaternary [12]. The stratigraphy of the study area is marked by the crust villafranchian that overcomes the thick Mio-Pliocene series. Villafranchian deposit consists of a limestone crust salmon [7], a calcareous crust or silts nodules. These deposits come in different facies: i) red clays: sometimes silty, ii) gypsum-rich crystals and often form the top of the series; the fine yellow sand; and iii) conglomerates or sandstone outcrops that often overcome the red clay gypsum. Occupied by Mio-Plioquaternary deposits, Zarzis peninsula is collapsed along a beam of normal faults corresponding to the major accident of southern Tunisia [16].

The upper Plio-quaternary aquifer (subject of this study) is formed by alternating deposition of gypsum, clay and sandstone. All these clastic deposits alternate with evaporate deposits, which represent the final stage of a great continental cycle [16]. The Miocene is a thick impermeable layer of marls, clays, and gypsum of Miocene-Pliocene age, which limits water infiltration. The lower aquifer is confined over all the coastal plain and its depth varies from 250 to 300 m. The general flow runs from the southwest to the northeast and converges to the Mediterranean Sea [11, 42]. This aquifer is recharged by water flowing (lateral leakage) from the Triassic aquifer system through the Medenine Fault [11, 26].

2.3. Water Sampling and Chemical Analysis

Twenty three groundwater samples were collected, in Marsh 2009, from the Zarzis aquifer. Well locations were shown in Figure **2**. The geographic coordinates and altitude of each well sampled were measured using eXplorist XL GPS Magellan. The depth of sampled wells ranges from 12 to 35 m. Total Dissolved Solids (TDS), Electrical conductivity (EC) and potential Hydrogen (pH) were measured in the field using a multi-parameter (C933 Multi-Parameter) Analyzer. The major ions (Na, K, Ca, Mg, Cl, SO_4 and $HCO_{3)}$ were analyzed using Ionic Chromatography (Methrohm 850 Professional IC). Results of the analysis of groundwater samples are shown in Table **1**.

2.4. HCA and PCA Analysis

Data were first statistically analyzed to check whether the parameters were normally distributed. In fact, in multivariate statistical and geostatistic analyses, normal distribution is preferred for optimal results and reliable interpretations of the results [5].

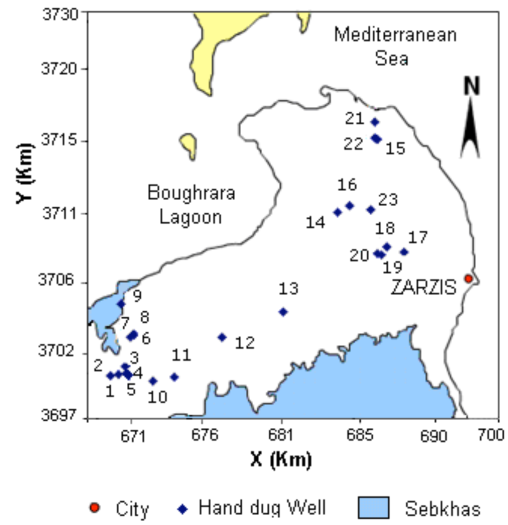

Figure 2: Groundwater sampling locations in study area.

Table 1: Geochemical Analysis of Sampled Water from Zarzis Peninsula Aquifer

N°	Coordinates						Measurement *in situ*				Major ions (mg/L)							IB %
	X			Y			EC ms/cm 25°C	pH	TDS (g/l)	PL (m)	Ca^+	Mg^+	Na^+	K^+	SO_4^{2-}	Cl^-	HCO_3^-	
	D	M	S	D	M	S												
1	10	39	3	33	26	26	8.75	7.6	7.4	8.5	624	393	989	26	2592	2059	268	-4
2	10	42	4	33	23	54	9.02	7.66	7.48	14	616	374	1023	23	2712	2130	97	-5
3	10	41	40	33	22	40	7.43	7.8	6.24	9	544	360	839	27	2832	1491	61	-4
4	10	41	42	33	22	18	7.19	7.73	6.12	2.5	448	417	816	27	2160	1384	167	3
5	10	10	47	33	24	10	7.4	7.76	6.2	3.5	560	321	839	23	2016	1526	186	2
6	10	47	53	33	24	15	10.68	7.63	8.36	1	536	328	1403	37	2352	2441	287	-3
7	10	48	12	33	24	37	9.43	7.59	7.56	3	624	259	1184	300	2184	2059	204	2
8	10	48	24	33	25	12	9.42	7.63	7.64	2	584	340	1207	370	2616	1988	237	2
9	10	48	17	33	25	18	7.21	7.67	6.12	2.5	528	340	897	331	2736	1242	13	5
10	10	48	33	33	26	2	7.3	7.79	6.16	3	544	405	828	257	2664	1526	143	1
11	10	48	41	33	26	8	10.65	7.71	8.8	4.5	544	537	1265	382	2640	2485	216	3
12	10	48	42	33	26	8	10.27	7.57	8.52	8	640	492	1092	432	2304	2556	216	3
13	10	48	6	33	27	37	9.56	7.69	6.88	9	408	422	1230	304	1008	2840	155	6
14	10	49	37	33	23	55	8.09	7.78	5.92	5	168	326	1173	312	1416	2059	215	2
15	10	50	45	33	24	7	8.17	7.59	6.4	2.5	540	225	480	370	1224	2094	158	-7
16	10	53	17	33	25	58	13.84	7.59	10.76	7	632	465	1840	425	2880	3692	122	-2
17	11	0	3	33	32	8	7.13	6.98	5.12	3	160	76	1265	70	38	2485	219	-2
18	10	59	24	33	31	50	6.94	7.65	5.08	5	336	134	1046	21	787	2130	103	-3
19	11	1	32	33	35	15	7.7	7.66	5.88	1	384	201	1092	22	1008	2556	109	-6
20	10	56	29	33	27	8	5.68	7.78	4	4	224	124	754	20	576	1349	115	3
21	11	2	49	33	29	51	6.42	7.78	4.72	1	368	192	885	33	840	1952	512	-5
22	11	1	54	33	30	6	10.95	7.51	8.96	1	816	259	1345	179	1704	2911	402	0
23	11	1	40	33	29	45	5.81	7.68	4.48	5	256	182	731	21	556	1704	164	-2

Hierarchical clustering Analysis (CA) is the most common approach in which clusters are formed sequentially, by starting with the most similar pair of objects and forming higher clusters step by step [37]. HCA uncovers intrinsic structure of a data set, without making a priori assumption about the data, in order to classify the objects of the system into categories or clusters based on their nearness or similarity [39]. HCA was applied to the Zarzis sampled waters in order to group the similar sampling sites in the resulted spatial dendrograms.

Principal component analysis (PCA) involves a mathematical procedure that transforms a number of correlated variables into a number of uncorrelated variables called principal components. The first principal component accounts for as much of the variability in the data as possible, and each succeeding component accounts for as much of the remaining variability as possible. The contribution of each factor at every site was computed and loadings and scores plots of first two principal components were constructed [18].

2.5. Geostatistical Analysis

Geostatistical tools allow spatial interpolation and therefore mapping spatial variability of TDS, EC and major ions using the kriging techniques. The theoretical fundamentals of the geostatistical methods are described elsewhere [15]. From a hydrogeochemical point of view, they are widely-used techniques [3, 8, 34, 40]. The first step in kriging is to calculate the experimental semi-variogram using the following equation (eq. 1).

$$\gamma(h) = \frac{1}{2N(h)} \sum_{i=1}^{N(h)} \left(Z(x_i) - Z(x_i + j)\right)^2 \quad (1)$$

In which γ(h) is the estimated value of the semivariance for lag distance h. N(h) is the number of experimental pairs separated by vector h. $Z(x_i)$ and $Z(x_i +h)$ are values of the variable Z at x_i and x_i+h, respectively.

The experimental semi-variograms were fitted to various theoretical models. The model that gave minimum standard error is chosen for further analysis [28]. The adequacy of the fitted models was checked on the basis of validation tests.

The ratio Nugget/sill and Root Mean Squared Error (RMSE) were used to express the extent of spatial autocorrelations of environmental factors. If the ratio Nugget/sill is low (<25%), the variable has strong spatial autocorrelations at a regional scale. A high ratio of nugget effect (>75%) plays an important role in spatial heterogeneity [13].

Root Mean Squared Error (RMSE) was computed. This parameter is often used to compare the performance of interpolation methods [32]. RMSE is computed according to (eq. 2).

$$RMSE = \sqrt{\frac{\sum_{i=1}^{N}[Z(x_i) - Z^*(x_i)]^2}{N}} \quad (2)$$

In which Z(xi) is the observed value and Z*(xi) corresponds to the predicted value of observation *i* in location x_i. RMSE is frequently used to evaluate errors in mapping aquifer parameters [11].

Kriging is a useful tool to estimate the groundwater parameters quality. Unlike other contouring techniques, it offers the possibility to quantify the estimation variance, defining thereby the precision of the resulting estimates [15]. The standard deviation map shows the confidence envelope that surrounds the estimated values. The kriging estimate is of the form (eq. 3)

$$Z^*(x_0) = \sum_{i=1}^{N} \lambda_i \; Z(x_i) \quad (3)$$

In which $Z^*(x_0)$ is an estimator of the unknown true value of the functional and λ_i are weighting coefficients determined in the kriging exercise.

3. RESULTS AND DISCUSSION

3.1. Summary Statistics

Basic statistics of the major ions concentrations, TDS and pH for all water samples are shown in Table **2**. The TDS values range from 4 and 10.76 g/l with a mean 6.73 g/l, indicating high groundwater salinity. Ca, Na, SO_4 and Cl show high values, indicating that theses ions govern salinity in Zarzis aquifer. Except for pH, kurtosis computed for all parameters ranges from -0.25 to 2.90, indicating a Gaussian distribution.

3.2. Water Quality

Figure **3** shows that TDS has a strong correlation with Cl, Na, Ca and SO_4 indication the contribution of these ions to groundwater mineralization. Therefore a high K values were showed in northern part of study area suggestion a dissolution of potassium salt from

Table 2: Descriptive Statistics from Chemical Analyses of Groundwater Samples

					Major ions (mg/L)						
	CE ms/cm 25°C	pH	TDS (g/l)	GWL (m)	Ca	Mg	Na	K	SO_4	Cl	HCO_3
max	13.84	7.8	10.76	14	816	537	1840	432	2880	3692	512
Min	5.68	6.98	4	1	160	76	480	20	38	1242	13
mean	8.48	7.64	6.73	4.57	481.91	311.83	1053.17	174.43	1819.35	2115.61	189.96
Var	3.73	0.03	2.68	10.96	28372.17	15115.88	81094.24	26675.8	790882	345617.3	11637.32
SD	1.93	0.17	1.64	3.31	168.44	122.95	284.77	163.33	889.32	587.89	107.88
Skewness	0.86	-2.85	0.50	1.14	-0.42	-0.16	0.57	0.32	-0.45	0.66	1.25
Kurtosis	0.65	9.38	-0.19	0.91	-0.45	-0.79	0.97	-1.65	-1.20	0.43	2.05

GWL: Groundwater level

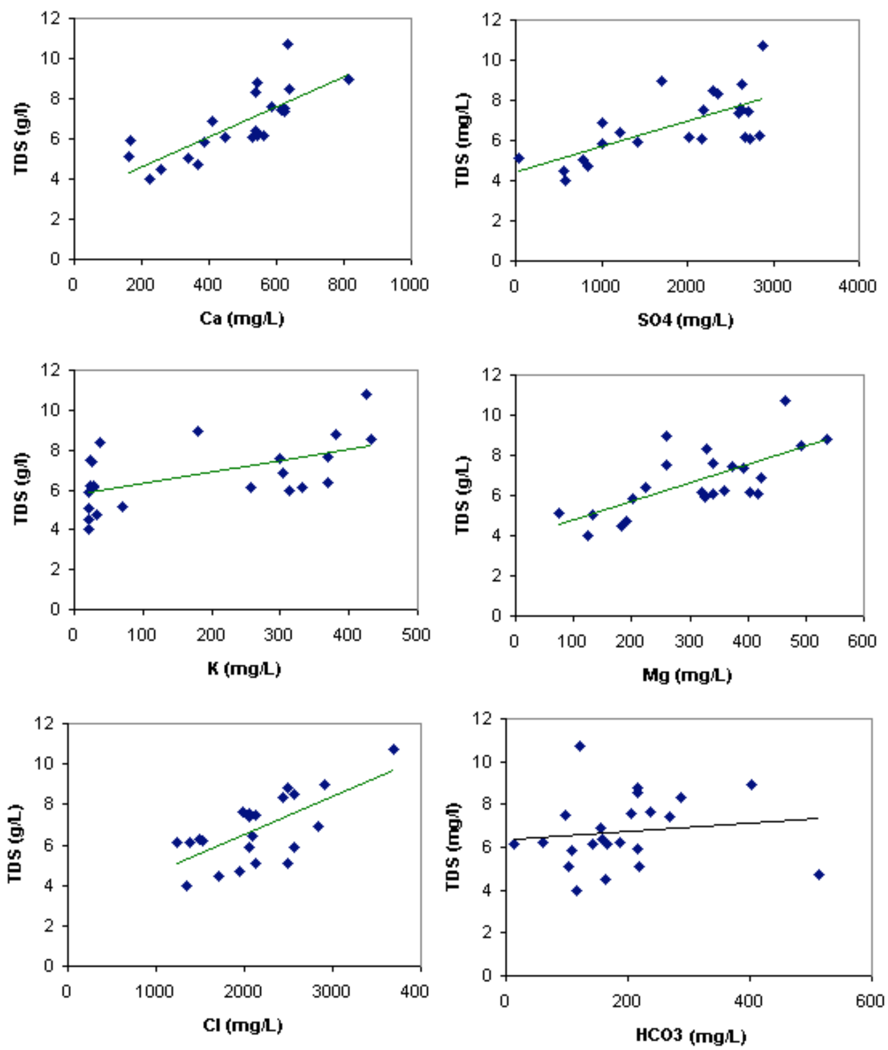

Figure 3: Relationship between TDS and major ions.

sebkhat El Melah. A strong correlation showed between Na-Cl and Ca-SO4 (Figure **4**) indicates that these ions evolve simultaneously and having probably the same origins. Figure **5**, pie diagram of median values of major ions, indicates that Cl, Na, SO_4 and Ca are the major ions controlling groundwater quality. These abundant ions seams result from rock-water interaction and controlled by regional geology.

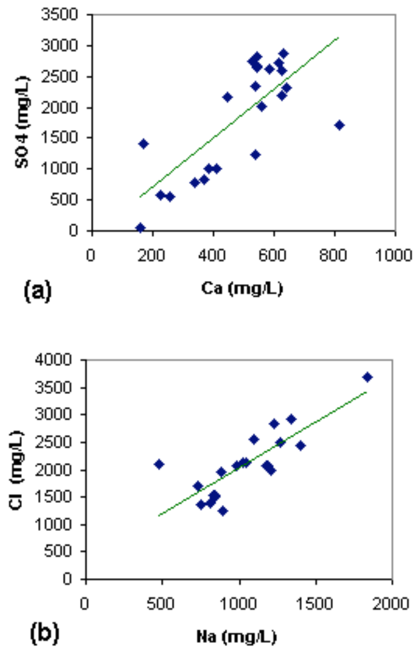

Figure 4: Relationship between a. Ca and SO_4, b. Na and Cl.

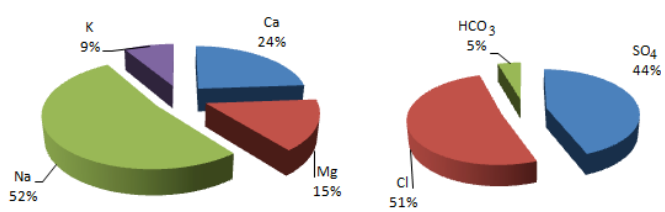

Figure 5: Pie diagram of median values of major ions of groundwater.

Figure **6**, relationship between $Ca/(HCO_3+SO_4)$ and Na/Cl, shows an excess of chlorine in groundwater from study area. However, the effect of base exchange has no significant effect. The calcium in groundwater comes largely from the dissolution of gypsum and calcium in groundwater is largely due to the dissolution of gypsum that original carbonate (Figure **7**).

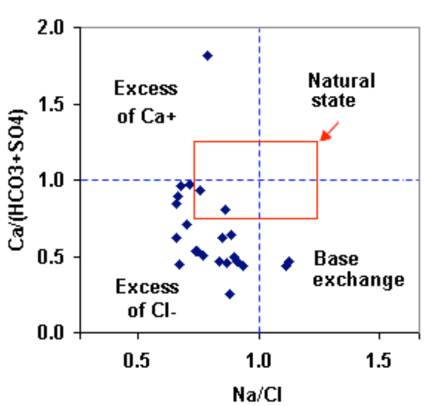

Figure 6: Relationship between $Ca/(HCO_3+SO_4)$ and Na/Cl.

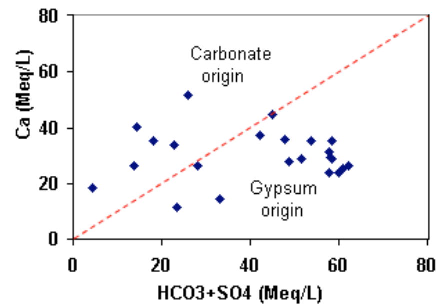

Figure 7: Relationship between Ca and HCO_3+SO_4.

DIAGRAMMES software [36] was used to plot Piper diagram of sampled groundwater. Piper diagram (Figure **8**) shows that the water facies are dominated by chlorinated and sulfated sodium calcium and potassium with dominance of Na-Ca-Cl-SO_4. The abundance of the major ions in groundwater from Zarzis aquifer is in the following order Cl>SO_4>Na>Ca> Mg>k>HCO_3. Geochemical analysis allowed us to conclude that groundwater chemistry is controlled by rock-water interaction and evaporation which are the dominant factors, leading to the poor quality of groundwater. Evaporation in arid areas greatly increases the concentrations of ions formed by chemical weathering of the rock, leading to higher salinity [33]. High concentrations of sodium, chloride, calcium and sulfate in groundwater may probably be related to dissolution of calcite ($CaCO_3$), gypsum ($CaSO_4$, $2H_2O$) and anhydrite ($CaSO_4$) while high concentrations of Na and Cl could be related to dissolution of halite (NaCl).

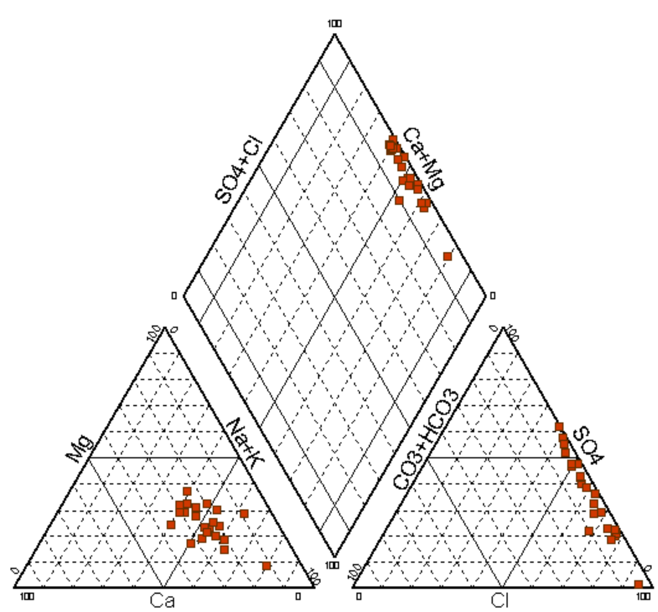

Figure 8: Piper diagram of groundwater from Zarzis shallow aquifer, showing chlorinated and sulfated sodium calcium and potassium with dominance of Na-Ca-Cl-SO_4.

3.3. Hierarchical Cluster Analysis (HCA)

Hierarchical cluster analysis (HCA) was applied to Zarzis aquifer groundwater quality data in order to categorize the different water samples. The dendrogram of groundwater quality data from the Q-mode Hierarchical cluster analysis (HCA) was plotted (Figure **9**). It is a presentation of the groundwater associations based on Euclidean distance. Figure 9 shows that two spatial groundwater types were distinguished from the dendrogram. HCA clusters together at low linkage distances samples with similar spatial characteristics and relationships are clustered together, whilst dissimilar samples are linked at higher linkage distances [30].

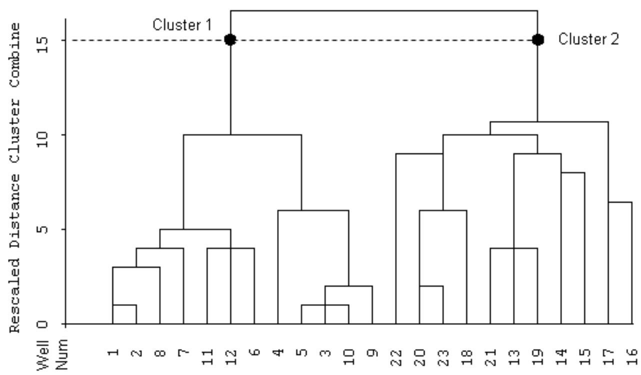

Figure 9: Dendrogram of groundwater quality from the Q-mode HCA including all water samples. The cluster analysis is based on the major ions parameters.

Dendrogram of groundwater quality from the Q-mode HCA (Figure **9**) shows that water samples were associated in two water groups. The first group represents the water samples (wells id. 1 to 12) located in the southern part of study area in which groundwater was a poor water quality and salinity exceeds 10 g/l. The second group characterizing wells located in the central and northern part of Zarzis aquifer (Wells id. 13 to 23), where dissolution of halite and gypsum represents the main processes governing the aquifer groundwater hydrochemistry.

3.4. Principal Component Analysis (PCA)

Principal Component Analysis (PCA) was performed for the groundwater quality data from the Zarzis aquifer (Figure **10**). PCA includes loading for the rotated component matrix, eigenvalues for each component, per cent and cumulative per cent of variance explained by each component, and communality indicating the proportion of variance of each variable controlled by the set of components [6]. Correlation matrix (Table **3**) indicates high values of communality for all chemical variables (between TDS and Ca, Mg, Na, K SO_4 and Cl). Table **4**, Rotated component matrix of the chemical data, reveals that the first three factors explain approximately 81.27% of total variance. The first two components explain 70% percent of the variance, respectively, and, thus, account for the majority of the variance in the original data set. However, component 3 explains 12.39% of the variance.

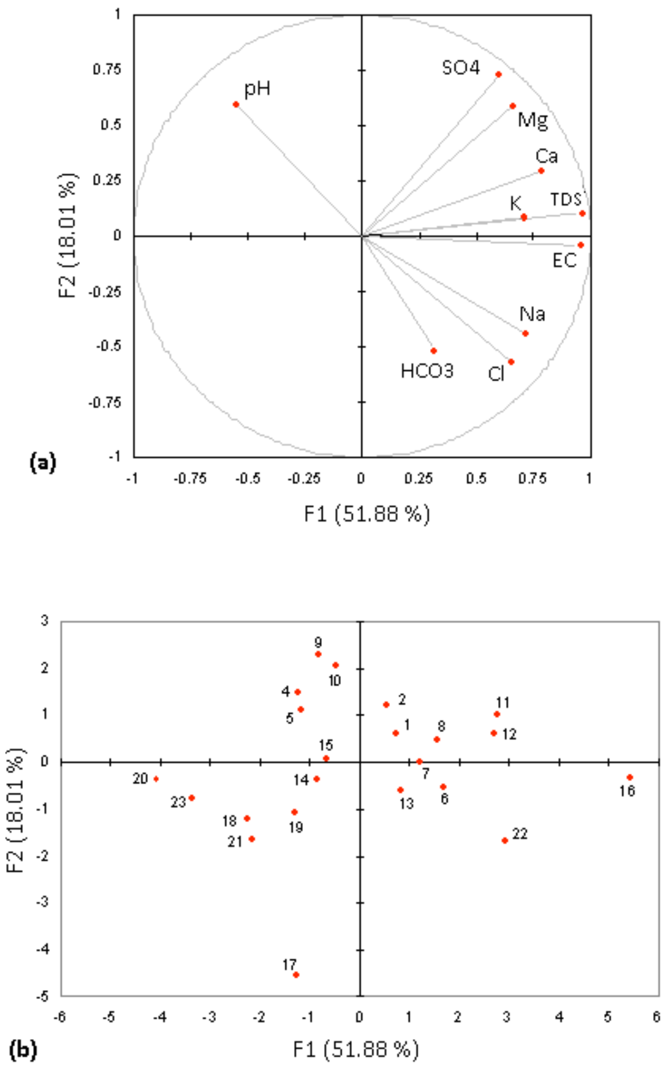

Figure 10: Projection of the variables in the first and second factorial plan.

The high positive loadings of EC, Na, Cl, and K on the first principal component (Figure **10**) suggest that the first principal component is associated with a combination of various hydrogeochemical processes and augment more mineralized water [41]. The concentration values of SO_4, Ca, Mg and pH show positive loadings on the second component while

Table 3: Correlation Coefficient among Major Ions, pH and TDS and EC in Groundwater of the Study Area

Variables	EC	pH	TDS	Ca	Mg	Na	K	SO_4	Cl	HCO_3
EC	1.00									
pH	-0.17	1.00								
TDS	0.97	-0.11	1.00							
Ca	0.64	0.09	0.77	1.00						
Mg	0.61	0.34	0.70	0.57	1.00					
Na	0.81	-0.34	0.71	0.23	0.30	1.00				
K	0.58	-0.04	0.56	0.33	0.52	0.33	1.00			
SO_4	0.53	0.32	0.68	0.75	0.80	0.23	0.36	1.00		
Cl	0.81	-0.41	0.68	0.26	0.21	0.81	0.38	-0.01	1.00	
HCO_3	0.15	-0.13	0.12	0.13	-0.11	0.18	-0.07	-0.18	0.25	1.00

Table 4: Rotated Component Matrix of the Chemical Data

Components	Initial eigenvalues			Sum of squares of factors for rotation		
	Total	% of variance	Cumulative %	Total	% of variance	Cumulative %
1	5.19	51.88	51.88	5.19	51.88	51.88
2	1.80	18.01	69.89	1.80	18.01	69.89
3	1.24	12.39	82.27	1.24	12.39	82.27
4	0.77	7.70	89.98			
5	0.63	6.25	96.23			
6	0.24	2.39	98.62			
7	0.11	1.06	99.68			
8	0.02	0.20	99.88			
9	0.01	0.11	99.99			
10	0.00	0.01	100.00			

HCO_3 concentration has moderate positive loadings on the third component. The highest concentrations of TDS observed on the first principal component is related to Cl, Na, SO_4 and Mg ions, which is an indication of rock-water interaction and evaporate dissolution.

Component 2 is defined as the hardness component. The high positive loadings of pH, Mg and Ca (Table **5**) are an indication of the hydrogeochemical effect [41]. Finally, component 3 is characterized by highly positive loadings in HCO_3. Component F3 is defined as the alkalinity.

3.5. Variographic Analysis

Variographic analysis was used to understand the spatial correlation between the different groundwater chemical parameters and select the best variogram model. The anisotropy was checked for TDS and major ions. For each semivariogram, sill, range and nugget were calculated and model was fitted. The ratio of

Table 5: Components Matrix

	Components		
	F1	F2	F3
EC	0.970	-0.181	-0.013
pH	-0.081	0.758	0.200
TDS	0.988	-0.018	0.046
Ca	0.736	0.328	0.337
Mg	0.740	0.515	-0.044
Na	0.731	-0.499	-0.099
K	0.636	0.063	-0.374
SO_4	0.685	0.640	0.054
Cl	0.687	-0.633	-0.073
HCO_3	0.110	-0.418	0.831

Table 6: Variographic Characteristics of TDS and Major Ions

	Model	Nugged effect (C_0)	Sill (C_0+C)	Range (A_0)	C_0/(C_0+C)
EC	Gaussian	0.53	20.84	14.3	3%
pH	Gaussian	0.01	0.26	0.78	4%
TDS	Gaussian	0.25	19.63	23.25	1%
PL	Exponential	1.29	10.47	1.73	26%
Ca	Gaussian	4.7	96.7	10.77	5%
Mg	Exponential	5.1	171.4	33.39	3%
Na	Gaussian	25	1060.9	32.04	2%
K	Exponential	0.27	0.6	10.8	45%
SO_4	Gaussian	9	277.1	14.67	3%
Cl	Gaussian	26	2303	31	1%
HCO_3	Linear	1.68	3.64	14.49	46%

nugget to sill (Nugget/sill) was used to express the extent of spatial autocorrelations of environmental factors (Table **6**). If the ratio is low (<25%), the variable has strong spatial autocorrelations at a regional scale. A high ratio of nugget effect (>75%) plays an important role in spatial heterogeneity in TDS and major ions [3, 13].

In order to simulate the spatial development of groundwater flow direction in the Zarzis Aquifer, a geostatistical analysis was considered. First, a variographic analysis was developed. The experimental variogram of the TDS (Figure **11**) shows an erratic behavior at the origin. This provides information on the existence of a drift. Therefore is necessary to improve the quality of the groundwater level estimation (GWL) to calculate the drive and check the model data distribution. Figure **12** shows a stationary drift with a zero mean. The distribution model data meets the criteria of universal kriging (eq. 4).

$$GWL(x) = m(x) + \varepsilon(x) \quad (4)$$

in which *ε(x)* is a random component, called residual, assumed to be intrinsic [17]. The term m(x) is a deterministic component, called drift; that contains the non-stationarity of *GWL(x).* It is equal to the expected value of GWL(x) at point x and varies with location x. When *m(x)* varies regularly, it can be represented locally as (eq. 5):

$$m(x) = \sum_{j=1}^{k} a_j f^j(x) \quad (5)$$

in which f^j (x) are some known functions, usually monomials, and a_j are some unknown coefficients. The representation of *GWL(x)* is valid for any physical phenomena that are continuous in space [27].

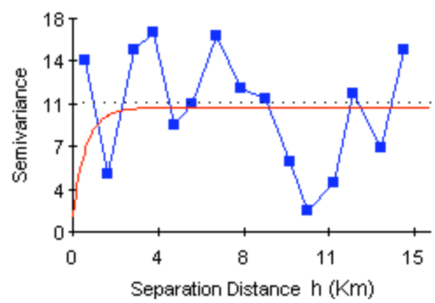

Figure 11: Experimental variogram and fitted model of the groundwater level.

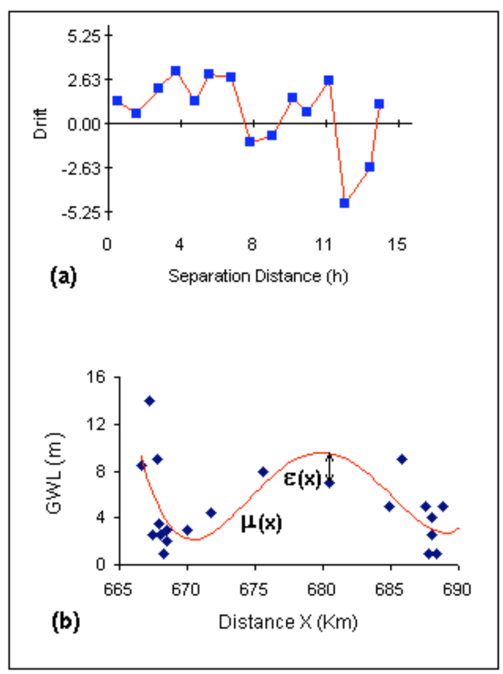

Figure 12: (**a**) Drift diagram (**b**) Universal kriging for the piezometric level.

Universal kriging (UK) [1, 27] is a special case of kriging with a changing mean, where the trend is modeled as a function of coordinates. Other authors [25, 39] also agree that the term Universal kriging should be reserved for the case where only the coordinates are used [14]. The basic idea in universal kriging is that the phenomenon studied, *z(x),* is viewed as a realization of a random function *GWL(x).*

The contour map of the kriged groundwater level (Figure **13**) was developed based on universal kriging using Easykrig 3.0 Matlab toolbox [9], with the lowest variance estimate. The kriged map seems to be more realistic. It is obvious from groundwater level contour kriged map (Figure **12**) that the regional groundwater flow direction is towards the coast line. The gradient of the water level varies from one area to another, depending on geological settings and the pumping rates.

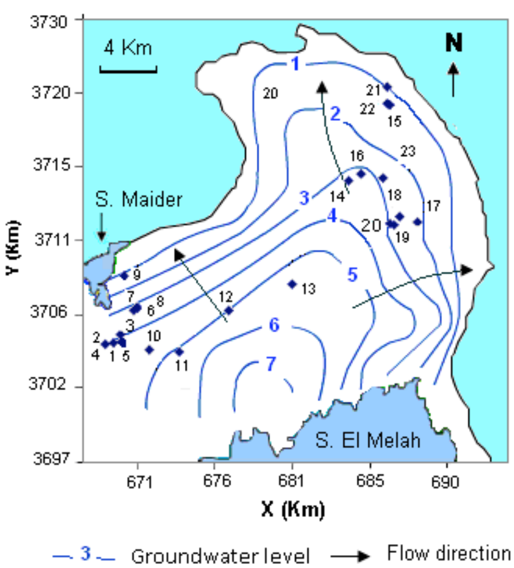

Figure 13: Contour map of kriged groundwater level (in 2009).

3.6. Total Dissolved Solids (TDS)

Variographic analysis was done to understand TDS's spatial development in Zarzis aquifer. TDS was modeled Gaussian (Figure **14.a**) and shows a low nugget effect, indicating a strong sampled autocorrelation. The best-fit model was selected based on cross-validation double-kriging between sampled and estimated values of the piezometric groundwater level (Figure **14.b**). The RMSE is 0.138 and the mean standard deviation is 0.224. The kriged map of TDS (Figure **15**) shows that TDS is highest in the south of study area, indicating the influence of salt depressions (Sebkhat El Melah et Sebkhat Maider) materialized by the dissolution of the halite and gypsum.

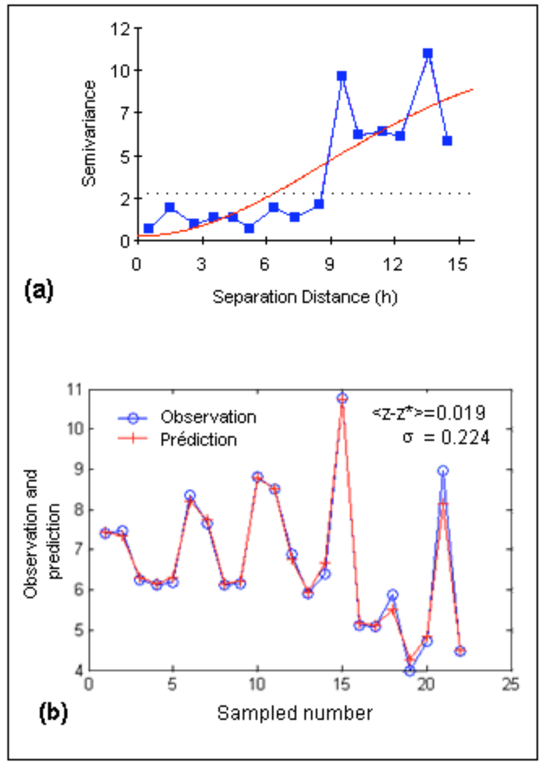

Figure 14: (**a**) Experimental variogram and fitted model of TDS, (**b**) Double kriging cross validation.

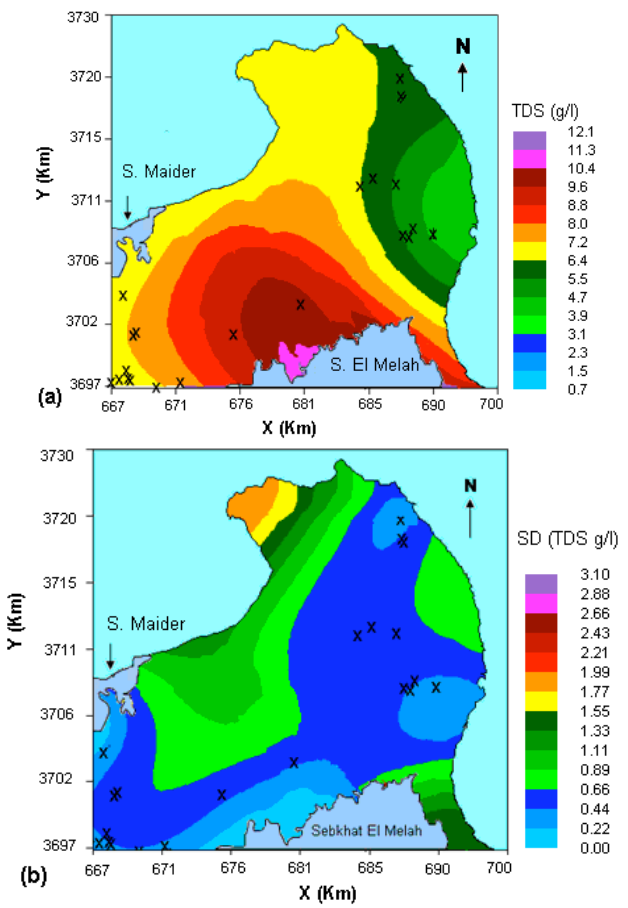

Figure 15: (**a**) Kriging map and standard deviation of TDS spatial development, (**b**) standard deviation of kriging map.

CONCLUSION

The study refers to Zarzis Peninsula shallow aquifer; climate, geology and geography are the factors on the origin of salinity. Several methods were used to determine the influence of the various parameters on the salinity of groundwater. The results of this study show that analysis of hydrochemical data using statistical techniques such as HCA, PCA and variographic analysis coupled with geochemical modeling can help elucidate the hydrologic and geologic factors controlling water chemistry on a regional scale.

The major ion chemistry data revealed that Na, Cl, Ca and SO_4 are the most predominant constituents. It's concluded that groundwater is controlled by rock-water interaction, saline depressions, aridity and increased evaporation. High salt concentrations are related to dissolution of NaCl, $CaCO_3$ and KCl in which Sebkhat El Maleh and sebkhat Maider (saline depressions) were the main salt sources.

Statistical analysis carried out by using Hierarchical Cluster Analysis and Principal Components Analysis of groundwater major ions provide confidence in identifying process controlling water mineralization and geochemical modeling results. Variographic analysis plays an important role in qualitative and quantitative predictions of salinity and groundwater level. It be concluded that TDS was correlated with groundwater flow direction and confirm the effects of saline depressions on groundwater composition.

The present study suggests that effects of the poor quality of groundwater on human health as well as on plant growth. A regional action plan for reducing salinity and improving water quality in Zarzis Peninsula becomes, therefore, an emergency.

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