Multivariate Statistical Analysis of Saline Water — A Case Study: Sabkha Oum LeKhialate (Tunisia)

Nasri Nesrine, Bouhlila Rachida, and Riadh Ahmed

***Abstract*—The hydrochemistry of the saline system in high arid environment is controlled by several processes including evaporation, water-rock interaction, precipitation /dissolution etc.**

Hydrochemical data of 80 wells from the catchment area of sabkha Oum leKhialate, southern Tunisia and 9 parameters (pH, TDS, Na^+, Ca^{2+}, SO_4^{2-}, Mg^{2+}, K^+, Cl^-, HCO_3^-) show that the abundance of major ions from the sabkha is as follows: Na>Ca>Mg>K and SO_4>Cl>HCO_3. Multivariate statistical analysis methods such us correlation analysis, principal component analysis (PCA) and hierarchical cluster analysis (HCA) were used to identify the geochemical processes controlling the chemistry of saline water in the catchment area of the sabkha.

HCA reveals four major water groups (C1-C4). Samples of the sabkha from clusters C1, C2 to C3 have Na-SO_4-Cl, Na-SO_4 and Na-Cl-SO_4 water type respectively. Samples from C4 show Ca-HCO_3-SO_4-Cl water type are located in recharge area. Using PCA, two factors account for 72.69 % of the total variance of the data set.

Results of statistical analysis reveal that the major source of sulfate sodium deposit is the process of evaporation, cationic exchange between Ca and Na in clay formation and mineral precipitation.

***Index Terms*—Hydrochemistry, saline system, statistical analysis, evaporation.**

I. Introduction

Water quality is controlled by many factors including climate, soil topography and water rock interaction. These factors lead to a variation in chemical composition and groundwater facies.

In literature, many studies have been focused in hydrogeochemical process of groundwater using statistical analysis [1]-[4]. Multivariate statistical methods permit to explain the correlation among a large number of variables and to reduce the number of variables into a small number of factors without loss of essential information [5].

These techniques constitute a useful tool for groundwater quality characterization [6], [7], for identification of the regional groundwater flow pattern [8] and investigation of groundwater contamination like trace elements [9].

Reference [10] applied hierarchical clusters analysis on brine evolution to show correlation between ions and suggest a non-marine type of saline system in Iran.

Hydrogeochemistry study of the groundwater evolution was attempted by [11] using factor analysis which allowed that sea water intrusion, weathering process and leaching of secondary salt to be the dominant factors controlling groundwater geochemistry.

The objective of this work is to identify the main process controlling the geochemical evolution of salt water using multivariate statistical methods such us correlation analysis, hierarchical cluster analysis (CA) and principal component analysis (PCA).

II. Materials and Methods

The study area Sabkha Oum LeKhialate, which covers about 52 km², is located in Southern East of Tunisia, a continental saline basin, characterized by an aridic climatic regime with mean evapotranspiration of 1100 mm/year and rainfall of 104 mm /year. The mean temperature is about 20.7 ℃.

The area is underlain by quaternary deposits and clay formation (Fig. 1). The substratum of the sabkha is mainly composed by Triassic clay of Beni Mhira formation. The mineralogy studies of the sabkha show that deposits contain variable quantities of gypsum ($CaSO_4$ $2H_2O$), thenardite (Na_2SO_4), glauberite (Na_2Ca $(SO_4)_2$, dolomite ($CaMg(CO_3)_2$ and quartz (SiO_2) [12]. The area is characterized by an enrichment of mirabilite (Na_2SO_4 $10H_2O$) deposits.

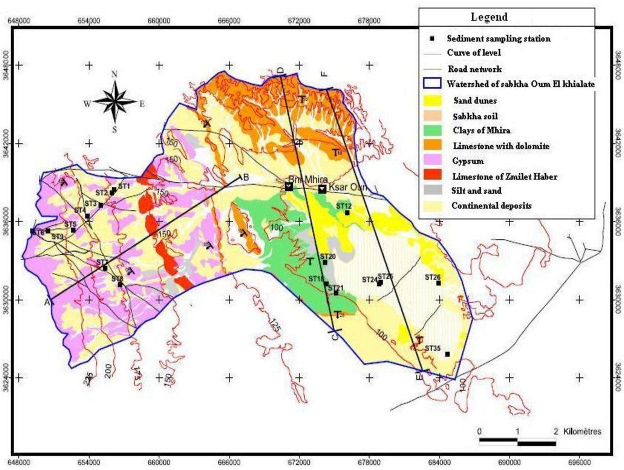

Fig. 1. Geological map of sabkha Oum Le Khialate [12].

The aquifer phreatic level is about 1 m. The direction of groundwater flow is south west to north east of the sabkha and the piezometric depression is in the center of the saline system (Fig. 2).

The water sample collected from the catchment study area

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Nasri Nesrine and Bouhlila Rachida are with Ecole Nationale d'Ingénieurs de Tunis, Laboratoire de Modélisation en Hydraulique et Environnement, Université de Tunis El Manar, 1002 Tunis, Tunisie (e-mail: nasri.hydro@gmail.com, bouhlila.rachida@enit.rnu.tn).

Riadh Ahmed is with Sté Chimique ALKIMIA (e-mail: riadh.ahmed@alkimia.com.tn).

show high concentration in Na, SO_4 in the center of the sabkha while Mg, Ca and HCO_3 present higher value in the western part of the area. The sabkha is characterized by high concentration of TDS (210g/l) (Fig. 3).

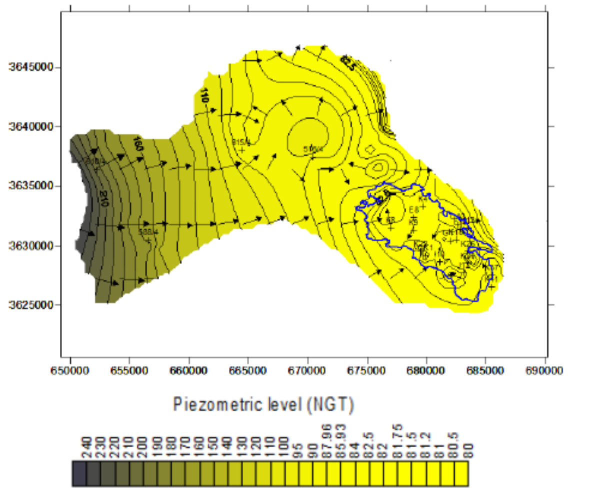

Fig. 2. Piezometric level of the catchment area of sabkha Oum LeKhialate.

The major hydrochemical facies identified using Piper trilinear diagram are Na-SO_4; Na-Mg-SO_4-Cl; Ca-HCO_3-SO_4-Cl water types (Fig. 4).

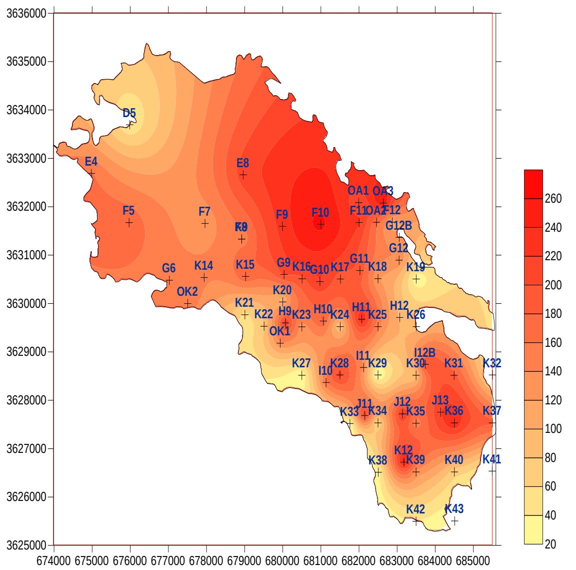

Fig. 3. Dry residue of the study area.

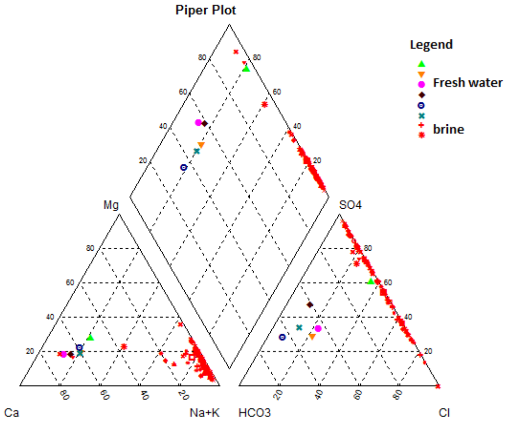

Fig. 4. Piper diagram.

Three multivariate statistical techniques: Correlation analysis, Hierarchical Cluster Analysis (HCA) and Principal Component Analysis (PCA) were used for the hydrogeochemical study in order to classify the water samples into distinct groups based on their hydrochemical characteristics. These methods can help to simplify and organize large data set to support meaningful insight [13]. The statistical analysis was performed using the software STATISTICA 8. All the data have been standardized applying standard statistical procedures.

III. Statistical Analysis

A. *Correlation Analysis*

Correlation analysis method is used to describe the degree of relation between hydrogeochemical parameters [14] which permit to identify the origin of solutes and the chemical evolution process of water samples.

Correlation coefficients values greater than 0.5 were considered efficient.

Table I show correlation coefficient results. TDS has strong correlation with Na^+, Mg^{2+}, SO_4^{2-} and Cl^- (0.65, 0.62, 0.88 and 0.62 respectively). These elements contribute to groundwater salinization.

SO_4 has a high positive correlation with Na and a low positive correlation with Mg and Cl and a negative correlation with Ca. This deduces that the principal source of sulfate is gypsum (Ca SO_4 $2H_2O$).

TABLE I: Correlation Coefficient of Element

Variable	Na	SO_4	Mg	HCO_3	Cl	Ca	K	TDS
Na	1	0.57	0.55	-0.44	0.43	-0.54	0.23	0.66
SO_4	0.57	1	0.29	-0.29	0.10	-0.60	0.42	0.85
Mg	0.55	0.29	1	-0.36	0.77	-0.52	0.60	0.62
HCO_3	-0.44	-0.29	-0.36	1	-0.36	0.36	-0.31	-0.40
Cl	0.43	0.10	0.77	-0.36	1	-0.36	0.75	0.52
Ca	-0.54	-0.60	-0.52	0.36	-0.36	1	-0.53	-0.66
K	0.23	0.42	0.60	-0.31	0.75	-0.53	1	0.45
TDS	0.65	0.82	0.62	-0.40	0.52	-0.66	0.75	1

Positive correlation between HCO_3 and Ca suggest that the presence of limestone and dolomite in the catchment area.

Positive correlation is obtained between Na^+-SO_4^{2}; Na^+-Mg^{2+}, Na-Cl and Mg^{2+}-Cl^-. These high correlations suggest that sulphate and magnesium derived from dissolution of gypsum and dolomite while sodium originates from cationic exchange between Na and Ca in clay formation during the process of evaporation.

B. Cluster Analysis

Cluster analysis technique is based on the classification of observations to group of homogenous data [15] into classes (clusters) on the basis of similarities within a class and dissimilarities between different classes. It is a powerful tool for the identification and the selection of homogeneous groups from the hydrochemical data [16]. There are two types of CA analysis: R and Q-modes.

The advantage of using the hierarchical method of cluster analysis applied in this paper is not requesting any prior knowledge of the number of cluster [16].

In the present work, CA was applied using the Euclidian distance as a distance measure between samples and Ward's method as a linkage rule for classification of the hydrogeochemical data of the sabkha Oum leKhialate.

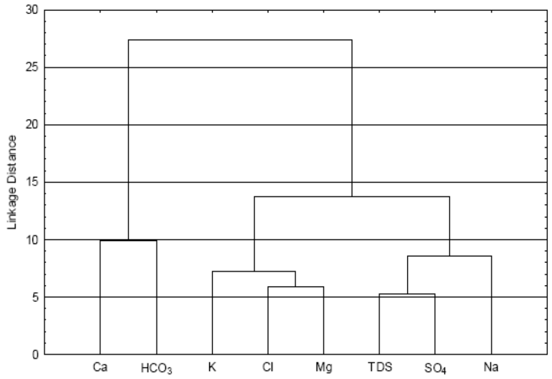

Fig. 5. Cluster dendogram for eight variables.

As shown in Fig. 5, eight variables were classified into three clusters. These groups are: (1) Na, SO_4 and TDS; (2) Mg, Cl and K; (3) Ca and HCO_3. Elements in the first group explain the highest mineralization according to the presence of minerals rich in sulfate sodium such us mirabilite (Na_2SO_4 $10H_2O$) where elements in group (2) and (3) are related to natural source of limestone and dolomite in the catchment area.

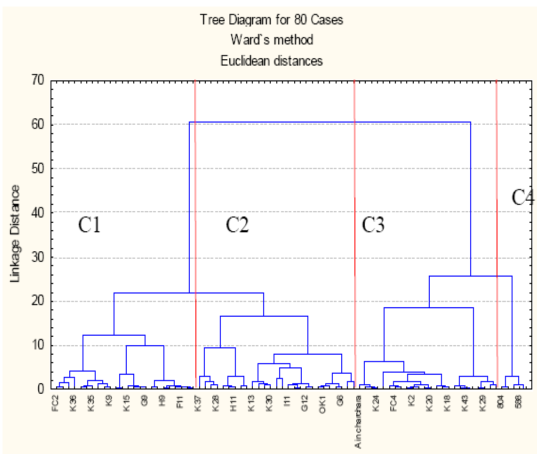

Fig. 6. Cluster dendogram of water samples.

Fig. 6 shows the classification of water samples into four groups (C1-C4), based on the visual observation of the dendogram.

C4 correspond to fresh water while C1-C3 corresponds to brine in the sabkha.

Cluster C3 and C4 have relatively higher linkage distance among the defined clusters while C1 and C2 have approximately lower linkage distance among all clusters.

The cluster C1 is characterized by Na-SO_4-Cl water type while C2 present Na-Cl-SO_4 water type. The cluster C3 has Na-SO_4 water type and finally C4 has Ca-Na-HCO_3-SO_4, Ca-HCO_3-SO_4-Cl.

C. Principal Component Analysis (PCA)

TABLE II: EIGEN VALUE, % TOTAL VARIANCE

Value number	Eigenvalue	% Total variance	Cumulative Eigen value	Cumulative %
1	4.580	57.260	4.580	57.260
2	1.234	15.435	5.815	72.695
3	0.833	10.416	6.648	83.112
4	0.615	7.693	7.264	90.805
5	0.435	5.448	7.700	96.254
6	0.215	2.691	7.915	98.9454
7	0.073	0.923	7.989	99.868
8	0.01	0.131	8.0	100

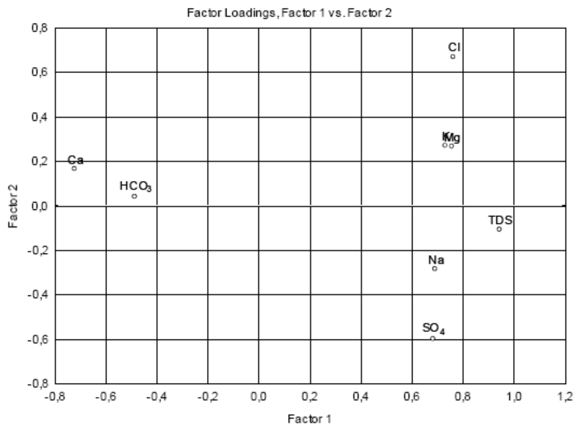

Fig. 7. Plot of loadings for the first two components.

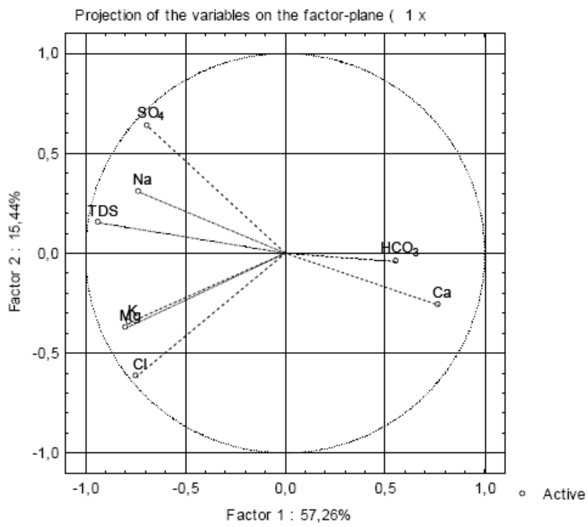

Fig. 8. Principal component analysis.

The PCA is a technique used to examine the underlying patterns for a large number of variables [17] and to determine the possible contributing factors in the hydrochemistry of waters samples [8].

Reference [18] applied PCA hydrochemical data to determine the main process controlling the hydrogeochemical evolution of groundwater.

The PCA is performed on eight major ions (Na^+, SO_4^{2-}, Mg^{2+}, Cl^-, K^+, HCO_3^- and TDS) and 80 water samples. It is applied to determine the processes of evolution for chemical composition in the sabkha Om leKhialate.

Table II presented the eigenvalue of parameters, their percentage of variance and cumulative of variance.

The eigenvalue exceed one; explain 57.26% of the total variance (Fig. 7 and Fig. 8).

Factor (F1) explains more 57 % of the total variance and is highly positive associated with Na, SO_4 and TDS. This factor is related to the dissolution of evaporites deposit (gypsum especially) and water-rock interaction. The source of sodium is the process of cationic exchange in clay formation. Therefore the factor F1 explains the salinization factor which is related to the process of evaporation in high arid environment and the dissolution of evaporite rocks.

Factor (F2) presents 15 % of the total variance and is characterized by positive loading in Ca and HCO_3.

The high positive loading in Ca suggests the importance of dissolution of carbonate rocks in the catchment area.

IV. Conclusion

Eighty water samples collected from sabkha Oum LeKhialate in southern Tunisia were analysed based on statistical analysis (correlation analysis, cluster and principal component analysis) to determine the geochemical processes controlling the saline water chemistry in high arid environment.

Evaporation process and cationic exchange reaction with dissolution of evaporites deposit are the major factor controlling the formation of sulfate sodium deposit.

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References

[1] R. P. Ashley and J. W. Llyod, "An example of the use of factor analysis and cluster analysis in groundwater chemistry interprestation," *J. Hydrology*, vol. 39, pp. 355-364S, 1978.

[2] M. Razack and J. Dazy, "Characterization of groundwater mixing in sedimentary and metamorphic reservoirs with combined use of Piper's principle and factor analysis," *J. Hydrology*, vol. 114, pp. 371-393, 1990.

[3] R. Reghunath, M. T. R. Sreedhara, and B. R. Raghavan, "The utility of multivariate statistical techniques in hydrogeochemical studies:an example from Karnataka, India," *Water Research*, vol. 36, pp. 2437–2442, 2002.

[4] M. Monjerezi, R. D. Vogt, P. Aagaard, and J. D. K. Saka, "Hydro-geochemical processes in an area with saline groundwater in lower Shire River valley, Malawi: An integrated application of hierarchical cluster and principal component analyses," *Applied Geochemistry*, vol. 26, pp. 1399–1413, 2008.

[5] A. T. Nadiri, A. A. Moghaddam, F. T-C. Tsai, and E. Fijani, "Hydrogeochemical analysis for Tasuj plain aquifer, Iran," *J. Earth Syst. Sci.* vol. 122, no. 4, pp. 1091–1105, 2013.

[6] V. Cloutier, R. Lefebvre, and R. Therrien, "Multivariate statistical analysis of geochemical data as indicative of the hydrogeochemical evolution of groundwater in a sedimentary rock aquifer system," *J. Hydrology*, vol. 353, pp. 294–313, 2008.

[7] H. Abderamane, M. Razack, and S. Vassolo, "Hydrogeochemical and isotopic characterization of the groundwater in the Chari-Baguirmi depression," *Environ Earth Sci*, vol. 69, pp. 2337–2350, 2013.

[8] K. S. Voudouris, N. J. Lambrakis, G. Papatheothourou, and P. Daskalaki, "An application of factor analysis for the study of the hydrogeological conditions in Plio-Pieistocene Aquifers of NW Achaia (NW Peloponnesus, Greece),"*Mathematical Geology*, vol. 29, issue 1, pp. 43-59, 1997.

[9] A. Kumar, S. Rout, and P. M. Ravi, "Spatial geochemical variation of major and trace elements in the marine sediments of Mumbai Harbor Bay," *Environ. Earth Sci.*, vol. 70, pp. 3057–3066, 2013.

[10] H. A. Torshizian, H. Mollai, M. Kalani, M. Ahwaz, and M. M. Javanbakht, "Hydrogeochemical analysis of the Siyah-kuh district playa brines Central Iran," *N. Jb. Geol. Paläont. Abh.*, vol. 253, no. 2-3, pp. 281–292, 2009.

[11] C. Singaraja, C. Thivya, S. Chidambaram, R. Thilagavathi, and M. V. Prasanna, "Statistical analysis of the hydrogeochemical evolution of groundwater in hard rock coastal aquifers of Thoothukudi district in Tamil Nadu, India," *Environ. Earth Sci.*, vol. 71, pp. 451-464, 2013.

[12] L. Baccar and M. A Louhaichi, "Hydrogeological survey of Sebkhet Oum El Khialat for the evaluation of the mining stock of Na_2SO_4," Final Report, p. 90, 2007.

[13] A. I. Mary, T. Ramkumar, and S. Venkatraman, "Application of statistical analysis for the hydrogeochemistry of saline groundwater in Kodiakarai, Tamilnadu, India," *J. Coastal Research*, vol. 28, issue 1A, pp. 89-98, 2010.

[14] G. Papatheodorou, N. Lambrakis, and G. Panagopoulos, "Application of multivariate statistical procedures to the hydrochemical study of a coastal aquifer: An example from Crete, Greece," *Hydrol. Process*., vol. 21, pp. 1482–1495, 2007.

[15] A. T. Nadiri, A. A. Moghaddam, F. T. C. Tsai, and E. Fijani "Hydrogeochemical analysis for Tasuj plain aquifer, Iran," *J. Earth Syst. Sci.* vol. 122, no. 4, pp. 1091–1105, 2013.

[16] L. Belkhiri, L. Mouni, and A. Tiri, "Water–rock interaction and geochemistry of groundwater from the Ain Azel aquifer, Algeria," *Environ. Geochem. Health*, vol. 34, pp. 1–13, 2012.

[17] A. Ugbaja, A. Edet, and O. Offiong, "Application of statistical methods in evaluating groundwater in parts of Mamfe Embayment, Southeastern Nigeria," *J. Geography and Geology*, vol. 4, no. 3, 2012.

[18] L. Belkhiri, A. Boudoukha, L. Mouni, and T. Baouz, "Multivariate statistical characterization of groundwater quality in Ain Azel plain, Algeria," *African J. Environ Sci. and Techn.*, vol. 4, no. 8, pp. 526-534, August 2010.

Nasri Nesrine was born in Tunisia, on August 25, 1981. She has the master degree in modeling in hydraulic and environment at National School of Engineering of Tunis. At the moment, she is a PhD student in the Laboratory of Hydraulic and Environment at National School of Engineering of Tunis. She focused in geochemical modeling of saline systems.

Bouhlila Rachida was born in Tunisia. She had her PhD degree in 1984 in mechanic at the National Polytechnic Institute of Toulouse and in 1999 she had her "Doctorat d'état ès-sciences" at the National School of Engineering of Tunis. She is currently a professor at the National School of Engineering of Tunis, University Tunis El Manar. She teaches porous media, hydrogeochemistry and hydraulic. Her research interests are: porous media, hydrogeochemistry and groundwater.

Riadh Ahmed was born in Tunisia on February 16, 1970. He was a engineer since 1995 at the National School of Engineering of Monastir. He has the master degree in industrial automatics at the National School of Engineering of Sfax. He is currently a PhD student at the National School of Engineering of Gabès. He had conducted industrial projects of ALKIMIA Group in Tunisia and abroad and currently is the Director of "Les Salines de Tataouine S. A" project to produce 115 000 MT of sodium sulphate project from Sebkhat Oum EL Khialate.