Desalination and Water Treatment
www.deswater.com

doi: 10.5004/dwt.2017.21507

92 (2017) 90–97
October

The hydrochemical characterization of the upper plains aquifers: case of the plain of F'kirina Ain-Beïda, Northeastern Algeria

Djoudi Salima[a,*], Houha Belgacem[b]

[a]*Faculty of Natural and Life Sciences, Department of Ecology and Environment, Laboratory Water, Environment and Renewable Energy, University of Abbes Laghrour, Khenchela, BP 40000, Algeria, Tel. +213 663837937; email: Djoudi.ecologie@gmail.com*
[b]*Laboratory Water, Environment and Renewable Energy, University of Abbes Laghrour, Khenchela, BP 40000, Algeria, email: bhouha@yahoo.fr*

Received 27 January 2017; Accepted 29 September 2017

ABSTRACT

Groundwater is one of the main sources of drinking water supply for the population and crops irrigation in the F'kirina area, which is located in the northeastern part of Algeria, characterized by a semi-arid climate. This work aims to evaluate the hydrochemical characteristics of an aquifer located between carbonated formations and salt lake (Garâat Ettarf). Hydrochemical, multivariate statistical, and thermodynamics techniques were used to investigate the hydrochemical evolution within the aquifer. A total of 45 groundwater samples were collected from this area during May 2015 and analyzed for various physical and chemical parameters. The results indicate that this water is classified as Ca-HCO_3 water types in carbonate outcrops as Ca-SO_4 and Cl-Ca type in the Plio-Quaternary filling in the direction of the Sebkha. The hydrochemical study shows that the electrical conductivity of the water ranges from 220 to 6,700 μS/cm. Chemical tracing had focused on the major elements and some traces to the process responsible for water mineralization acquisition. The intersection of the major elements with the chloride ion showed that the salinity of the water is due to water–rock interaction, cation exchanges and anthropogenic pollution. The principal component analysis reveals three factors that express 61.8% of the total variance in water quality datasets. The first factor is salinization, which shows strong associations between SO_4^{2-}, Cl^-, CE, M, TH, K^+, Ca^{2+}, Mg^{2+} and Na^+. The second factor represents the opposition of two poles, freshwater to polluted water, the first is constituted of bicarbonates HCO_3^- reflecting freshwater that opposes polluted water caused by nitrate. The third factor is determined in its positive part by temperature and in its negative part by pH. It should be noted that aquifers waters are oversaturated with respect to calcite, dolomite and aragonite, but they are rather undersaturated with respect to halite, gypsum and anhydrite.

Keywords: Groundwater; Water chemistry; Salinity; Saturation; F'kirina; PCA

---

1. Introduction

Groundwater is the major source of water for drinking, irrigation and industrial uses in many arid and semi-arid regions of the world [1]. Growing population, agricultural expansion and urbanization placed a heavy demand on water resources which are among the challenging issues especially in arid and semi-arid regions where the fresh water resources are limited [2]. Long-term and large-scale exploitation of mineral resources and rapid development of agricultural production dramatically contributed to the deterioration shallow groundwater ecological environment deterioration, aquifers destruction, groundwater level decline, surface runoff decrease, spring cutoff, groundwater pollution and so on [3].

Many workers have monitored the groundwater quality and tried to correlate it with the natural processes that affect groundwater quality such as precipitation chemistry nature

---

* Corresponding author.

and amount of recharge, type of rock/soil in the region, degree of rock weathering, etc. [4,5]. The presence of a salt lake hydraulically connected to groundwater also changes the water salinity by reversing the flow to groundwater due to overexploitation of this latter [6]. Studies of the major ions have been used to identify the hydrochemical facies of the water. Several researchers evaluated the groundwater chemistry and considered hydrogeochemical processes by developing geochemical modeling and adopting graphical methods for the interpretation of water quality indices [7–9].

The studied area is located within the semi-arid zones of Algeria, it is characterized by scarcity and uneven distribution of water resources and groundwater is the main supplier for domestic industrial and agricultural purposes. This paper aims to identify the main processes controlling the hydrochemistry of the groundwater of F′kirina, to meet this objective; we used geographic information system (thematic maps), conventional graphical plots, geochemical equilibrium modeling (PHREEQC) and statistics (correlation matrix, principal component analysis (PCA). The combination of hydrogeochemical tools and statistical analysis was applied to investigate the properties of groundwater among the sampling sites. The results of this study help to understand F′kirina aquifer and to give insights for a better management of the groundwater sources.

2. Materials and methods

2.1. Study area

The study area is located in the North of Algeria between 35°49′42′N to 35°8′30″N and 7°0′18″E to 7°5′6″E. This region covers an area of approximately 540 km². It is limited to the North by the line of water formed by Djebel El Galaa Kebira (1,246 m) and Djebel Ammamrat El Kebira (1,203 m), on the South by the line of water formed by Djebel Boutekhma (1,291 m) and Djebel Amer (1,259 m) to the East by the watershed line formed by Djebel El Medjifla (1,174 m) and Djebel Fedjidjet (1,291 m) and to the West by a large flat area marking the limit of the Constantine upper plains and by Garâat Ettarf (Fig. 1).

2.2. Geology and hydrogeology

The lithostratigraphy of the study area extends from Triassic to Quaternary series presented as follows (Fig. 2). In the study area, Triassic outcrop was observed Northeast and Southwest of Ain Delâa and F′kirina. Cretaceous formations are represented by marl-limestone with platelet limestone at the base; they also outcrop on the surface in the northern margin of Ain Beïda where they are highly fractured. The Eocene formations show marl and a carbonate sequence separated by slight sandstone. Miocene outcrops are of small dimensions and are distributed in the southern part of the plain. So it is a series composed of a set of marl-limestone at the top and a set of thick limestone at the center of the series.

Pliocene is made up of continental detrital deposits of sand, conglomerates, marls and reddish clays. Quaternary deposits covered most of the plains; these deposits are very varied. Sedimentation, however, is mainly made up of clay and marl.

The dominant formations in the study area (Fig. 3) are represented in their entirety by carbonate formations of the

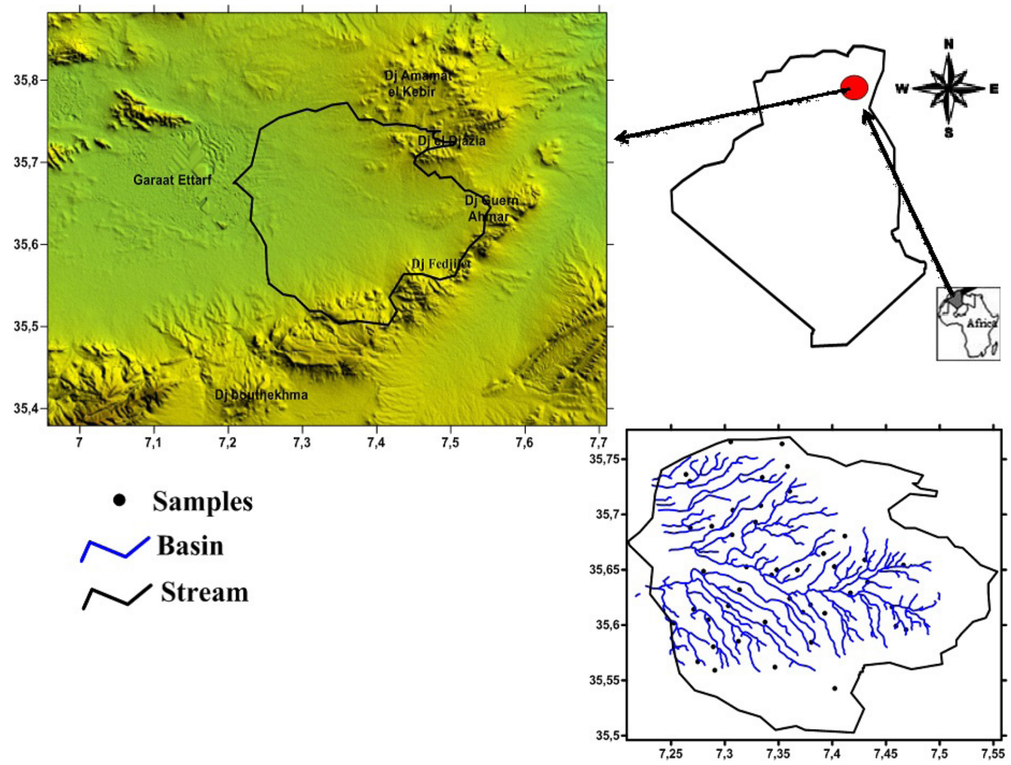

Fig. 1. Location of the study area.

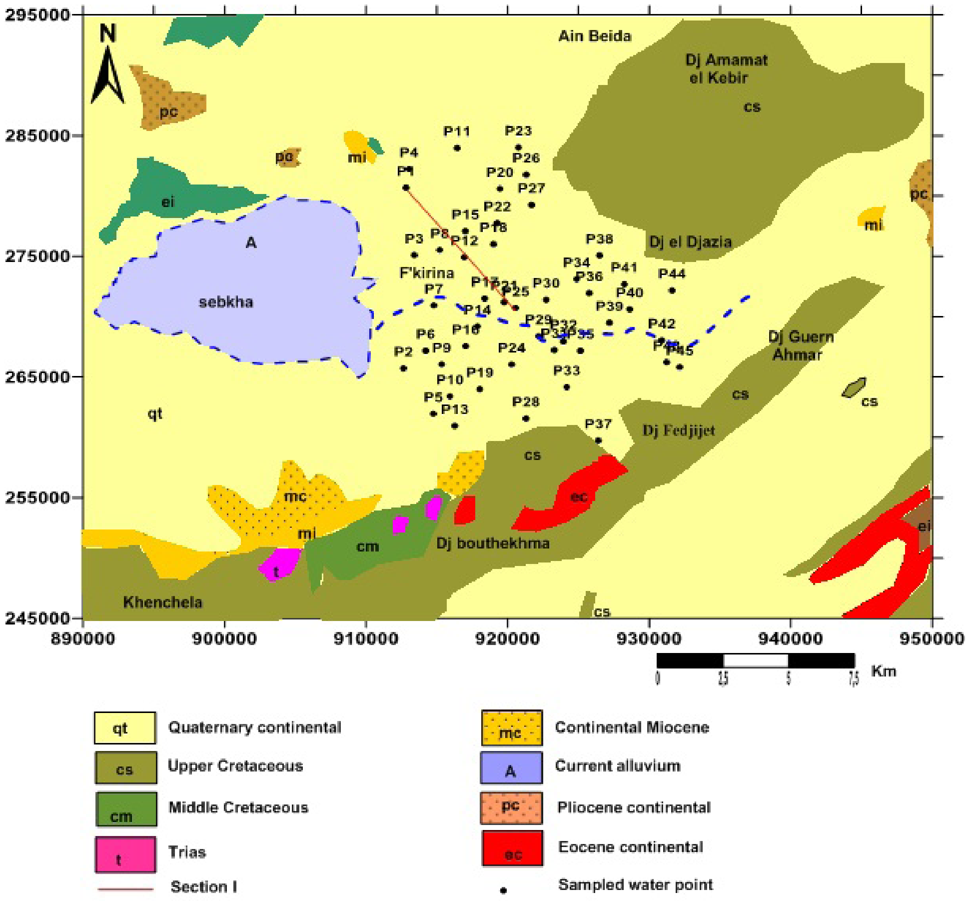

Fig. 2. Geological map of the study area.

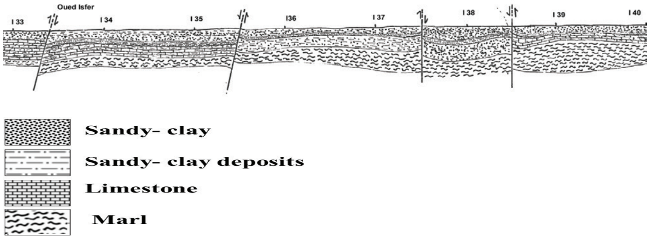

Fig. 3. Hydrogeological cross section located in the F'kirina plain Profile I (source: ANRH).

Upper Cretaceous covered by more recent age formations Mio-Plio-Quaternary; the training of the Upper Cretaceous formation is cracked and forms a supportive environment for the accumulation of groundwater [10].

2.3. Method of sampling and analysis

Groundwater samples can provide a lot of information on a water source such as nutrient content, pollution detection and bacterial counts. Water sampling is a technique used to analyze water from a variety of sources [11–13].

This study is based on analysis of 45 samples and the monitoring of the 21 piezometers covering the whole study area. Hydrochemical analyses were performed in LACILAP Laboratory (Ain M'lila, Algeria, May 2015) by the ion chromatography method. This method was used to determine concentrations of major elements; some physicochemical parameters were measured onsite such as water temperature, electrical conductivity (EC) and pH. Interpretation of the results (Table 1) is displayed numerically and graphically as saturation index (SI) by means of PHREEQC [14] and the chemical facies by the program DIAGRAM of the University of Avignon to better understand hydrochemical processes occurring in the aquifer.

3. Results and discussion

3.1. Piezometric study

The hydrodynamic study allowed us to characterize the flow and get a first grasp of the aquifers. This relationship has been further clarified in the hydrochemical study [15]. The piezometric study is in large part based on piezometric data collected during June 2012 campaign.

Analysis of the piezometric map (Fig. 4) shows that all water is drained by the Sebkha of Garâat at – Tarf which form the natural discharge area of the plain along an axis of direction SE-NW.

The disposition of the heads with respect to the limestone outcrops suggests that water comes from the carbonate formations.

3.2. Hydrogeochemical investigation

3.2.1. Electrical conductivity

EC is a measure of water capacity to convey electric current [16]. The value of EC may be an approximate index of the total content of dissolved substance in water. It depends upon temperature, concentration and types of ions present [17].

The spatial variation in measures of EC (Fig. 5) suggests that water salinity increases in the flow direction to reach very high values of EC and exceeds 1,500 µS/cm within the confines of the Sebkha. In limestone outcrops, the EC shows relatively low and consistent values.

3.2.2. Hydrochemical facies

As water flows through an aquifer it acquires a characteristic chemical composition as a result of interaction with the surrounding rock and soil. The term "hydrochemical facies" is used to describe the bodies of groundwater in an aquifer, which is different from their chemical composition [18].

The concept of hydrochemical facies is based on the assumption that the chemical composition of groundwater at any point tends toward chemical equilibrium with the matrix rocks under the prevailing conditions. Hydrochemical facies interpretations are useful tools for determining the flow patterns origins and chemical histories of groundwater masses [19].

The evolution of hydrochemical parameters of groundwater can be understood by plotting the concentration of major cations and anions in the Piper trilinear diagram [20].

The representation of the results of chemical analyses on the Piper diagram defines three families of water: starting from the limestone outcrops, water is Ca-HCO_3 type in the Plio-Quaternary filling passes through Ca-SO_4 water type and finishes as Ca-Cl water type near the Sebkha (Fig. 6).

3.3. Mechanisms controlling groundwater chemistry

Gibbs plot [21] is mainly used to understand the relationship between water compositions with their respective aquifer characteristics such as water–rock interaction, rainfall dominance (chemistry of precipitated water) and evaporation dominance (rate of evaporation) for groundwater chemistry. In the present study area the dominant anions (Cl and HCO_3) and cations (Na, K and Ca) are plotted against their respective total dissolved solids (Fig. 7). The Gibbs plot suggests that most of the samples fall into weathering zone and gives an indication of chemical weathering of rock-forming minerals influencing the groundwater quality by dissolution of rock through which water is circulating under the subsurface [22] and the chemistry of the groundwater is mainly controlled by complex geochemical mechanisms. The samples falling on evaporation dominance area may be due to semi-arid environmental climate conditions and surface contamination sources, primarily an excessive use of fertilizers in irrigation return flow. Industrial outflows and domestic discharges may also be the associated factors which ultimately lead to the increase in salinity with Na^+ and Cl^- due to evaporation. This study reveals that both evaporation and rock weathering (e.g., granitic rocks) are responsible for groundwater chemistry.

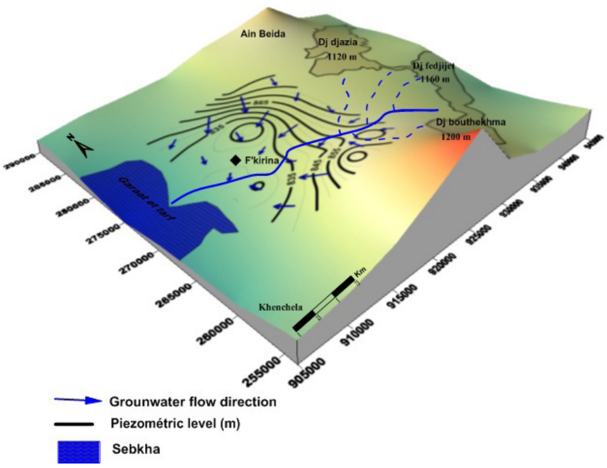

Fig. 4. Piezometric map of F'kirina aquifer in June 2012.

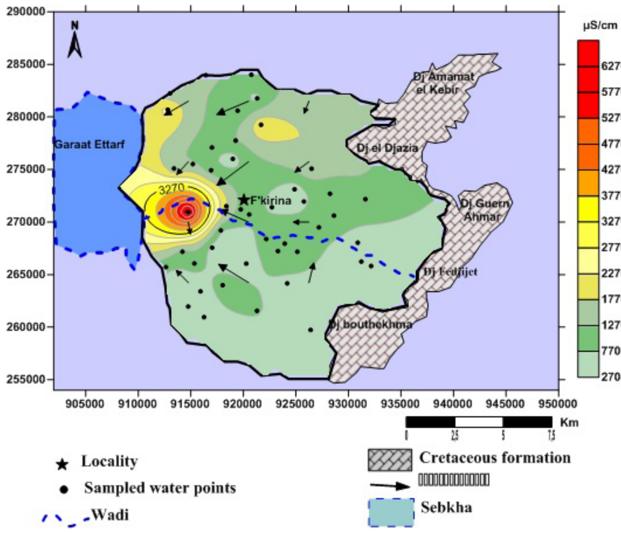

Fig. 5. Distribution map of electrical conductivity (µS/cm) in the study area.

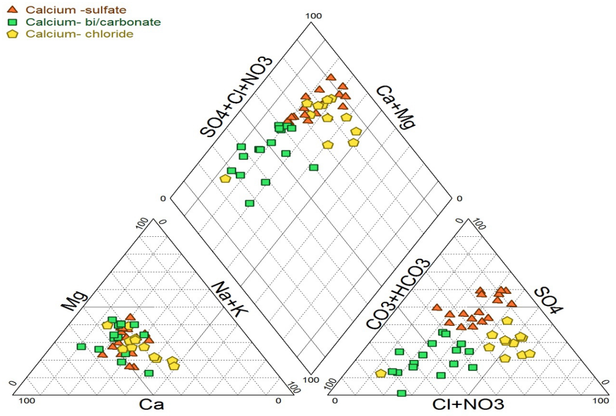

Fig. 6. Piper diagram of the groundwater samples.

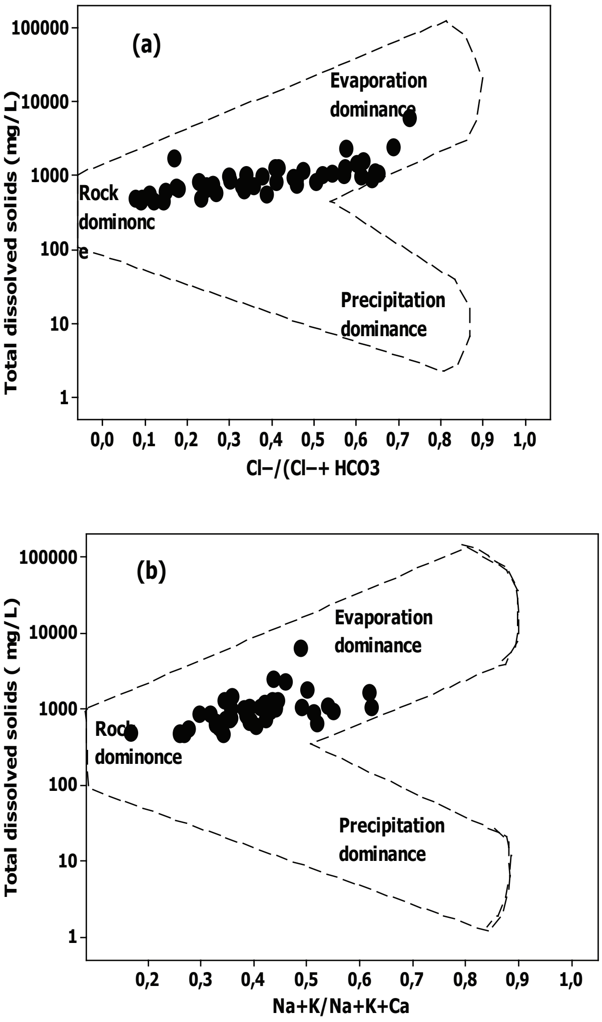

Fig. 7. Mechanism controlling the chemistry of groundwater (after Gibbs [21]): (a) dominant anion Cl^- and HCO_3^-, (b) dominant cation Na^+, K^+ and Ca^{2+}.

3.4. The saturation index

Chemical equilibrium of groundwater for a particular mineral can be identified by calculating saturation indices.

SI = log (IAP/Ks); where IAP is the ion activity product and Ks is the solubility product of the mineral. Saturation indices were calculated for calcite, halite, dolomite and gypsum. The saturation indices describe quantitatively the deviation of water from equilibrium with respect to dissolved minerals. If the water is exactly saturated with the dissolved mineral, SI equals zero; SI positive values indicate saturation, and negative ones indicate under saturation.

The use of WATEQ-F [23] program allowed us to calculate the SI (Fig. 8) of calcite, aragonite, dolomite, gypsum, anhydrite and halite (Table 2).

According to the saturation indices table, all groundwater samples are supersaturated with respect to calcite and dolomite and aragonite, whereas gypsum, anhydrite and halite are undersaturated, only the carbonate minerals tend to rush; however, the evaporate minerals are always in dissolution state.

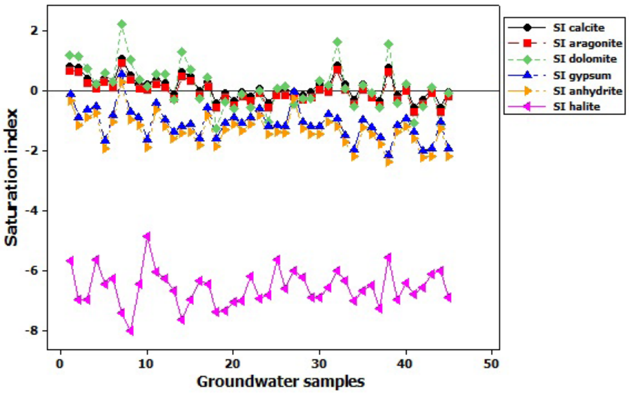

Fig. 8. Saturation index evolution (SI).

3.5. Origin of salinity

To highlight different mechanisms contributing to groundwater mineralization, bivariate diagrams of major elements and chloride were investigated (Fig. 9). The Na^+–Cl^- relationship has often been used to identify mechanisms responsible for the origin of water salinity in arid and semi-arid regions [24].

The relationship between Na^+ and Cl^- (Fig. 9(A)) shows that all the points are below the dissolution line. As the Na^+ content should balance the Cl^- content, the deficit in Na^+ is explained by the cationic exchange between the solution and the mineral resulting in a Na^+ adsorption and release of Ca^{2+} and Mg^{2+} (Fig. 9(F)).

The diagrams Ca^{2+}–Cl (Fig. 9(B)) and Mg^{2+}– Cl (Fig. 9(C)) show an enrichment of water in earth alkali. This indicates the phenomenon of cation exchange where the clay absorbs sodium and free calcium and magnesium in the solution. Calcium ion intake would also be attributed to the gypsum dissolution. The relationship between SO_4^{2-} and Cl^- (Fig. 9D) shows that all the points are above the mixing line of fresh and saline water. The enrichment of the sulfates points is related to the presence of evaporates dissolution of gypsum and/or an agricultural contamination. In the study area the infiltration of irrigation waters loaded with salt and fertilizers is facilitated by good permeability of the soil and a shallow depth of the water. The relationship between K^+ and Cl^- (Fig. 9(E)) indicates that the majority of points are located at the bottom of the mixing line except a few points that are closer to the line showing that the most likely origin of the K^+ is an agricultural pollution and the sylvite dissolution.

3.6. Statistical analysis

3.6.1. Correlation matrix

Multivariate statistical analysis was applied for 13 water parameters utilizing correlation matrix and PCA. First the relationships between different water variables were determined using Pearson's correlation coefficient (Table 3).

3.6.2. Principal component analysis

PCA is a powerful technique for pattern recognition that attempts to explain the variance of a large set of intercorrelated

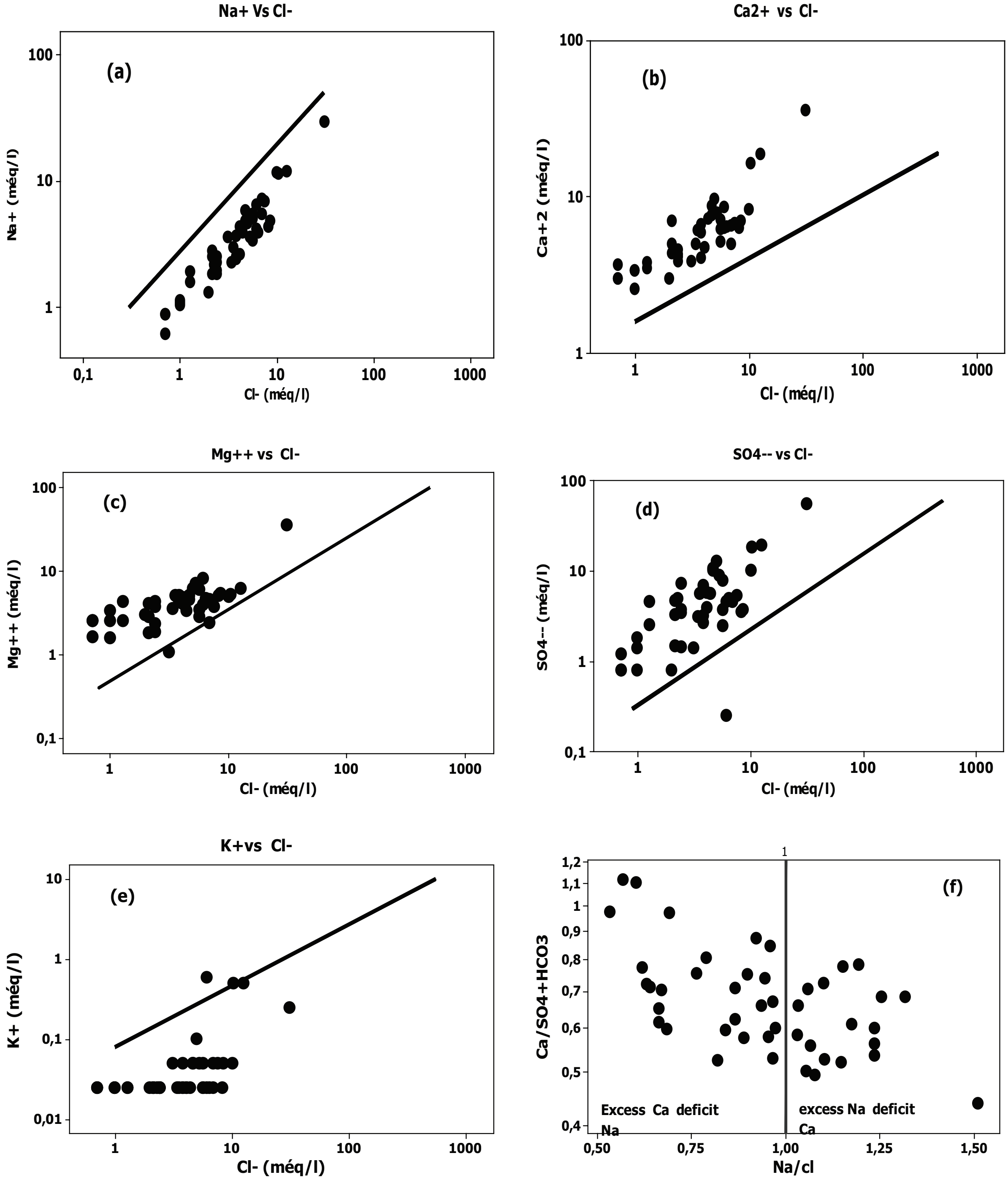

Fig. 9. Relationships between major elements in the analyzed groundwater samples: Na/Cl (**A**), Ca/Cl (**B**), Mg/Cl (**C**), SO_4/Cl (**D**), K/Cl (**E**) and Ca/SO_4+HCO_3/Na/Cl (**F**).

variables. It indicates association between variables, thus reducing the dimensionality of the dataset [25].

The projection of the variables and individuals on the factorial axes F1 – F2 allows extracting figures.

The factor F1 (Fig. 10) expresses 61.8% of the total variance and shows a positive correlation with the elements (Cl^-, SO_4^{2-}, CE, M, Ca^{++}, Mg^{++}, Na^+, K^+). It is an axis of mineralization. The screening of individuals (Fig. 11) shows that this group is well presented by the points (P7).

The factor F2 expresses 9.7% of the variance; it represents the opposition of two poles freshwater formed by the bicarbonates HCO_3 to the polluted water formed by nitrate ions.

The factorial axis F3 (Figs. 12 and 13) expresses 7.9% of the total inertia; it is determined in its positive part by temperature and negative part by pH. It is a contrast between the deep slow water to airy surface water.

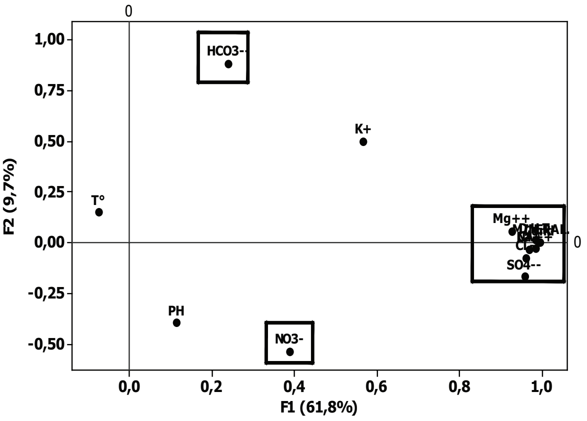

Fig. 10. Variables (axes F1 and F2: 71.5 %).

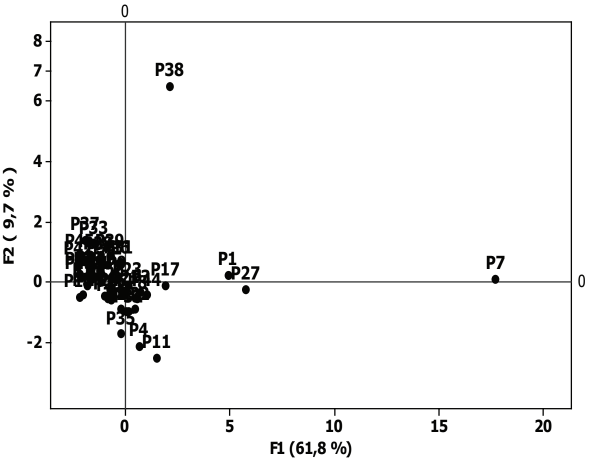

Fig. 11. Individuals (axes F1 and F2: 71.5 %).

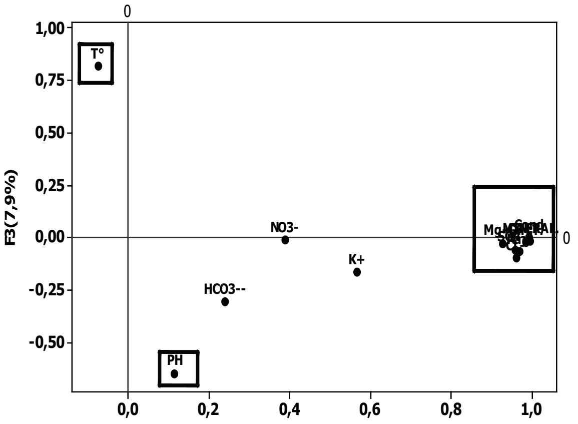

Fig. 12. Variables (axes F1 and F3: 69.7%).

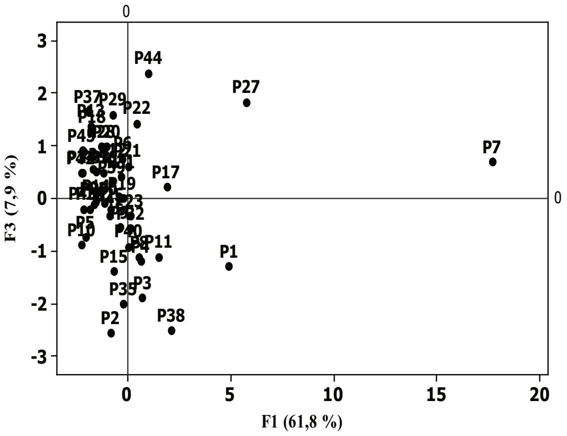

Fig. 13. Individual (axes F1 and F3: 69.7%).

Table 1
Statistical parameters of the chemical elements in groundwater

	Min	Max	Mean	SD	WHO
HCO_3, mg/L	101	1,046	229.578	138.760	–
SO_4^{--}, mg/L	3	2,645	278.711	412.770	400
Cl^-, mg/L	10	1,085	157.111	172.586	250
NO_3^-, mg/L	0	124	35.222	30.956	50
M, mg/L	372	5,704	945.156	831.624	–
Ca^{++}, mg/L	37	705	119.533	108.931	–
Mg^{++}, mg/L	2	412	41.600	59.298	0.50
Na^+, mg/L	1	665	85.644	108.036	–
K^+, mg/L	1	20	2.756	4.872	–
TDS, mg/L	451	6,100	1,047.38	884.460	–
EC, µS/cm	437	6,710	1,106.356	965.560	2,500
pH	6.7	8	7.323	0.302	6.5–8.5

Min, minimum; Max, maximum; SD, standard deviation.

Table 2
Statistical summary of thermodynamic speciation (saturation indices of some minerals calculations using PHREEQ

Variable	Min	Max	Mean	SD
Calcite	–0.560	1.080	0.126	0.382
Aragonite	–0.710	0.940	–0.022	0.382
Dolomite	–1.260	2.250	0.142	0.756
Gypsum	–2.150	0.550	–1.088	0.541
Anhydrite	–2.390	0.310	–1.326	0.540
Halite	–7.88	–5.58	0.566	–6.712

4. Conclusion

The study of hydrogeochemical characteristics of water in the F'kirina area was conducted from the combination of chemical, hydrogeological and statistical multivariable analysis methods. The hydrochemical study of the F'kirina plain showed that water is moderately to highly mineralized; conductivity is generally high and oscillates between 320 µS/cm and 6,500 µS/cm. The hydrochemical classification of water from Piper diagram shows that water fall into three water types. These are Ca-HCO_3, Ca-SO_4 and Ca-Cl types. The use of SI and binary diagram allowed us to understand that the waters mineralization process comes from water–rock interaction, evaporates leaching, agricultural pollution and cation exchange. The PCA and Gibbs diagram clearly reveal that the major factors affecting the chemical budget of water are anthropogenic activities

Table 3
Matrix of Spearman's correlation coefficients between the physicochemical parameters

	HCO_3^-	SO_4^-	Cl^-	NO_3^-	M	Ca^{++}	Mg^{++}	Na^+	K^+	TH	EC	PH	T°
HCO_3^-	1												
SO_4^-	0.041	1											
Cl^-	0.138	0.902	1										
NO_3^-	–0.319	0.364	0.411	1									
M	0.235	0.964	0.963	0.351	1								
Ca^{++}	0.190	0.961	0.936	0.423	0.982	1							
Mg^{++}	0.279	0.912	0.881	0.160	0.939	0.886	1						
Na^+	0.182	0.925	0.972	0.377	0.972	0.946	0.865	1					
K^+	0.600	0.410	0.469	0.308	0.535	0.589	0.354	0.523	1				
TH	0.238	0.966	0.937	0.307	0.990	0.974	0.968	0.934	0.491	1			
EC	0.241	0.962	0.960	0.326	0.998	0.973	0.949	0.969	0.510	0.990	1		
PH	–0.068	0.158	0.058	0.099	0.110	0.102	0.088	0.103	–0.064	0.098	0.129	1	
T°	–0.075	–0.052	–0.027	–0.113	–0.062	–0.065	–0.056	–0.011	–0.056	–0.063	–0.074	–0.260	1

and water–rock interaction. The use of the SI and binary diagram allowed us to understand the process of mineralization of waters comes from water–rock interaction. The leaching of evaporates agricultural pollution and cation exchange. The main component analysis and Gibbs diagram clearly reveal that the major factor affecting the chemical budget of water is due to anthropogenic activities in addition to rock–water interaction.

References

[1] K. Arina, U. Rashid, H. Haris, Hydrochemical characterization of groundwater in lower Kali watershed, Western Uttar Pradesh, J. Geol. Soc. India, 86 (2015) 195–210.

[2] M. Al-Ahmadi, Hydrochemical characterization of groundwater in wadi Sayyah, Western Saudi Arabia, Appl. Water Sci., 3 (2013) 721–732.

[3] Y. Qingchun, W. Luchen, M. Hongyun, Y. Kun, D. Jordi, Hydrochemical characterization and pollution sources identification of groundwater in Salawusu aquifer system of Ordos Basin, China, Environ. Pollut., 216 (2016) 340–349.

[4] R. Umar, F. Alam, Assessment of hydrogeochemical characteristics of groundwater in parts of Hindon–Yamuna interfluves region Baghpat District, Western Uttar Pradesh, Environ. Monit. Assess., 184 (2012) 2321–2336.

[5] S. Atal, P. Negrel, H. Pauwels, C. Mascre, S. Ahmed, Double correction technique for characterizing groundwater quality zones: a case study from granitic setting, India, Water Qual. Exposure Health, 2 (2011) 133–146.

[6] A. Boudoukha, D. Khammoudj, L. Djabri, Consequence of an overexploitation of aquifers in semi-arid countries: the case of the superficial aquifer El Eulma (Eastern Algeria). Groundwater in Mediterranean countries, Pub. Inst. Geol. Min. Esp. Series Hydro. Aguas Subt., 17 (2006) 459–465.

[7] M. Jalali, Salinization of groundwater in arid and semi-arid zones: an example from Tajarak, Western Iran, Environ. Geol., 6 (2007) 1133–1149.

[8] N.C. Mondal, V.P. Singh, V.S. Singh, V.K. Saxena, Determining the interaction between groundwater and saline water through groundwater major ions chemistry, J. Hydrol., 388 (2010) 100–111.

[9] E. Wanda, M. Monjerezi, F. Mwatseteza, L.N. Kazembe, Hydrogeochemical appraisal of groundwater quality from weathered basement aquifers in Northern Malawi, Phys. Chem. Earth Parts A/B/C, 361 (2011) 1197–1207.

[10] ANRH études de formation aquifère de la région de Fkirina, Agence national des resources hydrique, 2012.

[11] Z. Chen, Z. Bai, B.K. Sinha, Ranked Set Sampling Theory and Applications, Springer, New York, 2004.

[12] A.G. Dehnavi, R. Sarikhani, D. Nagaraju, Impact of arsenic on environmental geochemistry of South East of Kurdistan Iran, Nature Environ. Pollut. Technol., 10 (2011) 473–480.

[13] R. Sarikhani, Z. Kamali, Ghassemi, A. Dehnavi, R.Z. Sahamieh, Correlation of lineaments and groundwater quality in Dasht-e-Arjan Fars SW of Iran, Environ. Earth Sci., 72 (2014) 2369–2387.

[14] D.L. Parkhurst, C.A.J. Appelo, PHREEQC for Windows Version 1.4.07, A Hydrogeochemical Transport Model, US Geological Survey Software, Washington, 1999.

[15] R. El Moukhayar, M. Bahir, P. Carreira, Estimation of groundwater recharge in arid region through hydrochemistry and isotope case study Kourimat basin morocco, Larhyss J., 23 (2015) 1112–3680.

[16] WHO (World Health Organization), Guidelines for Drinking-Water Quality, Vol. 1, 4th ed., World Health Organization, Geneva, 2006.

[17] J.D. Hem, Study and Interpretation of the Chemical Characteristics of Natural Waters, 3rd ed., USGS Water Supply Paper 2254, 1985, pp. 117–120.

[18] P. Ravikumar, R. Somashekar, A geochemical assessment of coastal groundwater quality in the Varahi river basin Udupi district Karnataka state India, Arabian J. Geosci., 6 (2013) 1855–1870.

[19] S. Ramin, G.D. Artimes, A. Zeinab, K. Nasrollah, Hydrochemical characteristics and groundwater quality assessment in Bushehr Province, SW Iran, Environ. Earth Sci., 74 (2015) 6265–6281.

[20] A.M. Piper, A graphic procedure in geochemical interpretation of water analyses, Trans., Am. Geophys. Union, 25 (1994) 914–923.

[21] R.J. Gibbs, Mechanisms controlling world water chemistry, Science, 17 (1970) 1088–1090.

[22] S. Selvakumar, K. Ramkumar, N. Chandrasekhar, N.S. Magesh, S. Kaliraj, Groundwater quality and its suitability for drinking and irrigational use in the southern Tiruchirappalli district, Tamil Nadu. India, Appl. Water Sci., 7 (2017) 411–420.

[23] L.N. Plummer, B.F. Jones, A.H. Trusedall, WATEQ-A FORTRAN IV version of WATEQ, a computer program for calculating chemical equilibrium of natural waters, Vol. 76, U.S. Geological Survey Water Resources. Washington, D.C., 1976, Revised (1978, 1984), pp. 13–61.

[24] A. Guendouz, A. Moulla, W. Edmunds, K. Zouari, P. Shand, A. Mamou, Hydro geochemical and isotopic evolution of water in the complex terminal aquifer in the Algerian Sahara, Hydrogeol. J., 11 (2003) 483–495.

[25] P. Ravikumar, R. Somashekar, Principal component analysis and hydrochemical facies characterization to evaluate groundwater quality in Varahi river basin Karnataka state, India Appl. Water Sci., 7 (2017) 745–755.