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Multivariate statistical analysis of the groundwater of Ain Djacer area (Eastern of Algeria)

Said Bencer[1] · Abderrahmane Boudoukha[1] · Lotfi Mouni[2]

Abstract The intensive exploitation of groundwater resources in the region of Ain Djacer has greatly influenced the hydrochemical functioning of the superficial aquifer. This has resulted in a general decline of the piezometric level of the groundwater, a mineralization of water and calcium facies near limestone and sodium chloride in the center of the plain in liaison with the lithology. To highlight the hydrochemical processes of groundwater, a study by major ions were analyzed in 21 groundwater samples collected from this aquifer during the month of March 2004. Multivariate statistical techniques and cluster and principal component analysis were applied to the data on groundwater quality, with the objective of defining the main controls on the hydrochemistry at the plain. These statistical techniques have shown the presence of three salinity groups with increasing importance according to the direction of flow. The initial facies on the limits as well as infiltration areas is bicarbonate. In the center of the plain, water becomes charged with sodium (Na) and chlorine (Cl) in connection with the dissolution of salt formations. The presence of nitrates is related to agricultural activity.

Keywords Multivariate statistical · Principal component analysis · Cluster analysis · Hydrochemistry · Groundwater · Algeria

Introduction

The groundwater quality is influenced by many factors, such as the chemistry of infiltration water, the geological nature of the reservoir rock, the decomposition of organic matter, and anthropogenic factors (Frape et al. 1984). The dissolution of minerals from the surrounding rock in the water is the dominant factor controlling the chemical composition of these waters. Some minerals such as carbonates and evaporates rapidly dissolved and significantly changed the chemical composition of the water, while others such as mineral silicates dissolved more slowly and therefore have less effect on the chemical composition of water (Garrels and MacKenzie 1967). The temperature also has an essential role in the chemical composition of groundwater (Hem 1989; Boudoukha and Athamena 2012). Most studies as Hartman et al. (2005), Adams et al. (2001), and Alberto et al. (2001) showed that the groundwater chemistry is mainly a function of the interaction between water and mineralogical composition of the aquifer. Hydrochemical processes occurring within this system are dissolution, precipitation, and ion exchange. These phenomena occur along the groundwater flow and also depend on the residence time which controls the evolution of the chemical composition of groundwater (Apodaca et al. 2002). Several statistical techniques have been applied to study, assess, and characterize the chemical changes in groundwater as cluster analysis (CA) and principal component analysis (PCA)

✉ Abderrahmane Boudoukha
boudoukha_abderrahmane@yahoo.fr

Said Bencer
bencersaid@gmail.com

Lotfi Mouni
lotfimouni@gmail.com

[1] Laboratory of Applied Research in Hydraulics, University of Batna 2, Road of Constantine, 05078 Fesdis-Batna, Algeria

[2] Laboratory of Management and Valuation of Natural Resources and Quality Assurance. SNVST Faculty, University of Akli Mohand Oulhadj, 10000 Bouira, Algeria

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(Belkhiri et al. 2010). Meng and Maynard (2001); Farnham et al. (2003) used FA to discuss geochemical evolution and mineralization and groundwater contamination. Additionally, the CA was also used to interpret the hydrochemical data based on factor scores, for example, (Suk and Lee 1999; Reghunath et al. 2002; Kim et al. 2005). This technique was used to study the chemical evolution of water along the groundwater flow by many researchers such as (Plummer et al. 1990; Rosenthal et al. 1998; Eary et al. 2002; Güler and Thyne 2002).

Several techniques have been applied to study, assess, and characterize the chemical changes in groundwater, such as thermodynamic equilibrium that defines the chemical evolution of groundwater. For this, the tendency of chemical forms between the dissolved phase and the inorganic phase was examined by the saturation index. This expresses the degree of chemical equilibrium between water and the inorganic matrix in the aquifer and can be considered a measure of the dissolution and/or precipitation in the study of water–rock interaction (Gibbs 1970; Drever 1997). The use of code PHREEQ-C allows calculating the saturation indices of some carbonate and evaporating minerals (Parkhurst and Appelo 1999).

The objective of the present work was to characterize the chemistry of groundwater and determine the origin of the chemical elements present in the waters of the plain of Ain Djacer in Algeria, by using the multivariate statistical techniques.

Materials and methods

Study area: general overview

The investigated area is located in the East of Algeria. Most of inhabitants (more than 20,000 inhabitants) are centered on the town of Ain Djacer. The principal activity in this area is the production of cereals (barley and corn), and its climate is semi-arid. Ain Djacer region is centered on latitude 35°49′ 50″N and longitude 6°00′16″E. The catchment area of Ain Djacer covering an area of 210 km^2 is a relatively flat terrain and very low slope. The topography of the plain is nearly flat with a slope not exceeding 2 %, and the highest altitude is 865 m. This morphology allowed the installation of a low temporary hydrographic network. This hydrographic network is drained by a set of topographic depressions further north creating an endorheic drainage network. The region is characterized by annual rainfall of about 260 mm and an annual mean temperature 15.9 °C (Mebarki 2009). The establishment of water balance according to Thornthwaite formula over in the past 20 years (1993 to 2013) in the station of Batna airport shows that this region is in deficit.

Geological and hydrogeological setting

The geological setting of the area was established from a detailed surface geological map of the area (Wildi 1983; Vila 1980). Five main units are identified as follows: (1) Triassic saliferous, (2) Jurassic carbonate, (3) Cretaceous carbonate, (4) Mio-Pliocene, and (5) Quaternary. Figure 1. Triassic saliferous diapir is found in the northern part of the study area in Chouf Rherab. This unit is composed by crushed ice and hand complex limestone dolomitic. Jurassic and Cretaceous carbonate formation are formed by dolomitic limestone and sandstone, sometimes with thick marl layers of about 550-m thick. The Mio-Plio-Quaternary formation is a heterogeneous continental detrital sedimentation. It is corresponding to red clay, sometimes gypsum overcome by lacustrine limestones, conglomerates, and alluvium. The thickness of this formation varies between 300 and 500 m (Boudoukha 1988). Mineralogically, most of the soils are dominated by kaolinite, illite, smectite, and chlorite, typical for most arid and semi-arid soils. The presence of smectite suggests specific sites for sodium adsorption (Belkhiri and Mouni 2013).

Tectonics of the region led to the formation of a syncline filled with detrital elements, of Mio-Plio-Quaternary age. The superposition of several tectonic phases allowed the Triassic carbonate formations staked Triassic and development of severe fracture network direction southwest, northeast, northwest, and southeast.

The studied area is situated in the alluvial plain of the Mio-Plio-Quaternary showing a heterogeneous continental detrital sedimentation. This aquifer is constituted by very varied deposits such as alluvial fans, silts, calcareous crust, conglomerates, and gravels. This shallow groundwater mainly occurs 10–100 m below the surface, 10 m in these limits and 100 m in the center of the plain. The substratum of the shallow groundwater is formed by clays and marls; sometimes are gypsum of Mio-Pliocene. The pumping tests on different wells showed high transmissivity (10^{-4} m/s) indicating high yields. Groundwater is recharged by vertically infiltrating meteoric water in the basin and by stream water coming from different reliefs surrounding the depression intermountainous of the plain. Since 1997 to 2013 (Chabour 1997; Bencer 2005; Ziani 2009), the water table has maintained the same structure, characterized by the presence of two zones, the first in the west with a west–east flow and the second in the east with an east–west flow. The morphology of the water table was imposed by the syncline structure of the substratum. These two flows converge towards the center of the plain for being drained to the north. This piezometric state shows that the aquifer has a limitation of inflow from carbonate massifs which surround the plain to the west, south, and east and a discharge to the north.

Fig. 1 Hydrogeological map of
Ain Djacer area
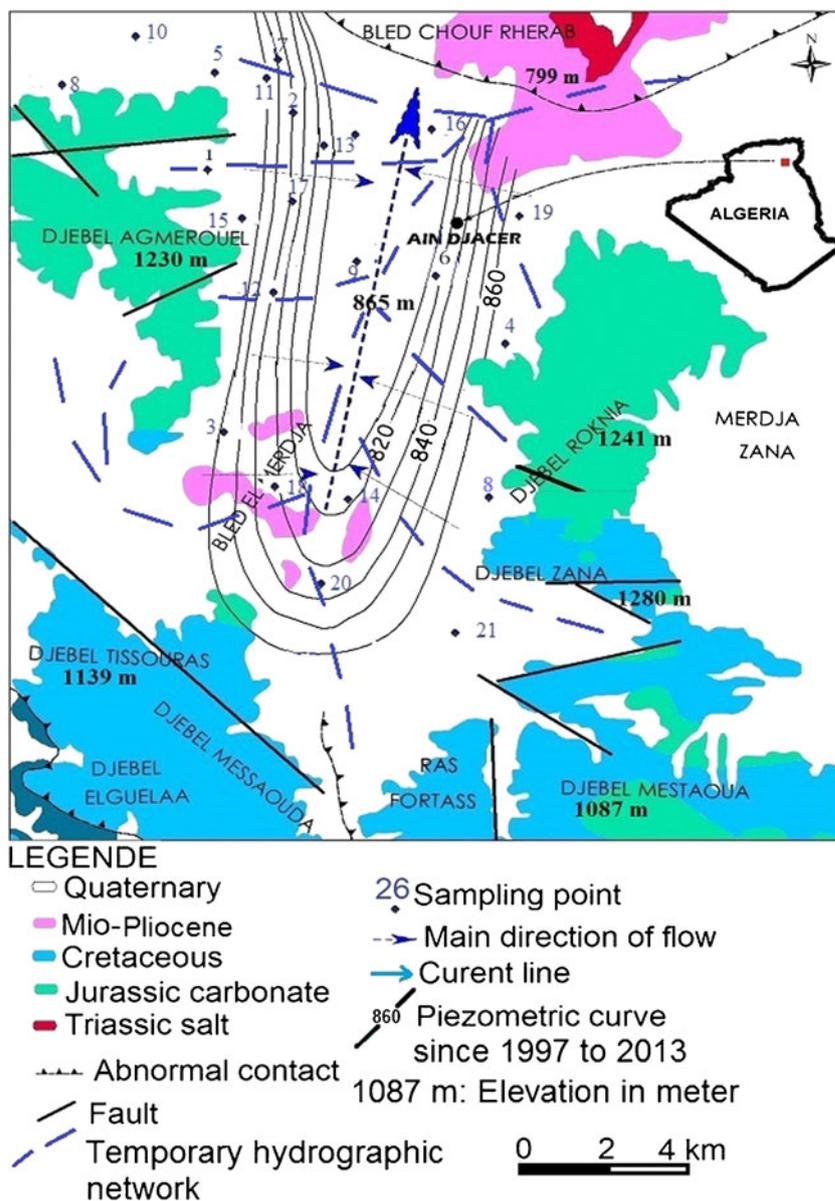
Sample collection and methods

To examine the evolution of the physicochemical parameters, 21 samples were taken during the month of March 2004. The samples were collected after pumping for 15 min after stabilizing the temperature of the water to remove groundwater stored in the hydraulic structure. These samples were collected using two polypropylene bottles washed with acid. Each sample was immediately filtered on site through 0.45-μm filters on acetate cellulose. Filtrate for cations analyses was transferred into 100-cm^3 polyethylene bottles and immediately acidified to pH <2 by the addition of Merck™ ultrapure nitric acid (5 ml 6N HNO$_3$). Samples for anions analyses were collected into 250-cm^3 polyethylene bottles without acidified. All the samples were stored in

an ice chest at a temperature of <4 °C and later transferred to the laboratory of the National Agency for Water Resources of Constantine and stored in a refrigerator at a temperature of <4 °C until they have been analyzed (within 1 week). Immediately after sampling, pH is measured in the field using a multi-parameter WTW (P3 MultiLine pH/LF-SET). Chemical elements have been analyzed: calcium (Ca^{2+}), magnesium (Mg^{2+}), sodium (Na$^+$), potassium (K$^+$), chloride (Cl$^-$), bicarbonate (HCO$_3^-$), sulfate (SO$_4^{2-}$), nitrate (NO$_3^-$), and total dissolved solids (TDS). The samples were analyzed following the methods outlined in the American Public Health Association (APHA 2005). The accuracy of the chemical analysis was verified by calculating ion-balance errors where the errors were generally within 10 %.

The thermodynamics that was conducted using the code PHREEQ-C was used to calculate the saturation indices (SI) and tackle speciation minerals. The calculation of the SI was conducted according to formula 1.

$$SI = \log \left(IAP \Big/ K \right) \tag{1}$$

where IAP is the ion activity product of the mineral water reaction and K is the thermodynamic equilibrium constant. The SI minerals are used to evaluate the state of saturation of the water and control the chemistry and equilibrium with the solid phase (Drever 1997).

The principal component analysis (PCA) was also applied to the treatment of these chemical data. Although PCA is an exploratory and descriptive method, the aim of the treatment is to identify the main factors that control the chemistry of the groundwater (Dagnélie 2006). This multivariate statistical method has been widely applied to investigate the phenomena of the environment across the world (Anazawa and Ohmori 2005; Güler and Thyne 2004; Laaksoharju et al. 1999) and in Algeria (Belkhiri et al. 2010; Tiri et al. 2014). These multivariate statistical tools were used successfully to study the hydrogeochemical processes (Duffy and Brandes 2001; Khedidja and Boudoukha 2014). This work deals with the force of multivariate techniques to characterize hydrochemical variations in the area.

There are two types of cluster analysis (CA): 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 (Belkhiri et al. 2010). CA comprises a series of multivariate methods which are used to find true groups of data (Belkhiri et al. 2010). In clustering, the objects are grouped such that similar objects fall into the same class (Danielsson et al. 1999). The hierarchical method of cluster analysis, which is used in this study, has the advantage of not demanding any prior knowledge of the number of clusters, which the nonhierarchical method does. A review by Belkhiri et al. (2010) suggests Ward's clustering procedure to be the best, because it yields a larger proportion of correct classified observations than do most other methods. Hence, Ward's clustering procedure is used in this study. As a distance measure, the squared Euclidean distance was used, which is one of the most commonly adopted measures (Fovell and Fovell 1993). 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 Ain Djacer area.

All statistical computations were made using Excel 2010 (Microsoft Office ®) and STATISTICA 6 (StatSoft, Inc. ®).

Multivariate analysis of the lake groundwater quality data set was performed through CA and PCA.

Results and discussion

Hydrochemical analysis

Examination of the statistical characteristics of the chemical analyses (Table 1) shows that the pH values ranging from 7.09 to 7.95, which indicate that the groundwater show a low alkalinity. It is known that the process of buffering calcite and dolomite is dominant for the pH range 6.5 to 7.5 (Blowes and Ptacek 1994; Geller et al. 2000). The values of pH measured for 21 groundwater samples are in accordance with the norm. Salinity represented by the TDS (Fig. 1) increases from the west to the east in the western part and east to west in the eastern part; it passes from 490 mg/l on the limits to 2640 mg/l in the center of the plain. This is in line with the flow that allows the concentration of elements in the rows and axes underground flow. The Ain Djacer plain is an area where a flow is "horizontal" which one has a relatively small change in topography, going from 1200 m on the recharge zone to 850 m in the plain over a distance nearly to 6 km. In general, this gradient allows a gradual increase in the mineralization of groundwater and to spend a carbonate facies to a saliferous facies. This typology is observed in water table moving to less horizontal due to the low gradient of groundwater which allows increasing water–rock interaction.

Alkalinity varied from 238 to 342 mg/l with the mean value of 293 mg/l. Na^+ varied from a low of 137 mg/l to a high of 638 mg/l with the mean value of 379 mg/l, and 86 % of samples exceeded the maximum acceptable concentration of Na^+ for drinking water (200 mg/l). K^+ ranged from 2 to 13 mg/l with the mean value of 9.36 mg/l, and 5 % of samples exceeded the maximum acceptable concentration of K^+ for drinking water (12 mg/l). Ca^{2+} ranged from 78 to 358 mg/l with the mean value of 177.5 mg/l, and 43 % of samples exceeded the maximum acceptable concentration of Ca^{2+} for drinking water (200 mg/l). Mg^{2+} varied from 33 mg/l to 146 mg/l with the mean value of 75.2 mg/l. Cl^- varied from 36 to 1053 mg/l with the mean value of 512.4 mg/l, and 47 % of samples exceeded the maximum acceptable concentration of Cl^- for drinking water (500 mg/l). SO_4^{2+} ranged from 195 to 693 mg/l with the mean value of 420 mg/l, and 52 % of samples exceeded the maximum acceptable concentration of SO_4^{2+} for drinking water (400 mg/l). (OGRA 2011). Higher concentrations of Na^+, Cl^-, and SO_4^{2+} in the area of Ain Djacer indicate a dissolution of evaporate minerals.

The high concentration of nitrate is probably due to wastewater leakage from industrial activities, urbanization, and agricultural practices. NO_3^- varied from 3 to 125 mg/l with the mean value of 36.7 mg/l. Strong content is recorded in the

Table 1 Hydrochemical parameters of shallow groundwater in the study area. All values are in mg/l, except pH and variation coefficient in %

No. of wells	pH	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	Cl^-	SO_4^{2-}	HCO_3^-	NO_3^-
1	7.80	940	260	59	243	11	195	385	256	3
2	7.65	1500	110	77	270	10	675	355	299	64
3	7.53	2110	296	140	638	9	930	465	287	33
4	7.95	960	358	146	301	9	1053	603	317	23
5	7.80	1970	242	125	470	13	940	525	268	28
6	7.60	2070	152	115	400	10	940	508	250	65
7	7.56	2110	122	57	464	10	319	365	299	82
8	7.70	880	158	62	150	12	438	410	287	20
9	7.35	2490	78	48	170	11	53	199	342	125
10	7.45	1380	268	88	479	10	675	671	238	19
11	7.42	1290	228	98	450	8	435	693	256	46
12	7.65	1250	156	53	350	11	425	302	293	56
13	7.36	1750	224	82	452	12	1005	621	287	76
14	7.10	1480	164	61	478	11	585	495	293	62
15	7.15	890	350	67	340	6	427	345	317	15
16	7.09	2640	96	53	233	5	180	280	311	82
17	7.19	1350	122	52	289	2	217	195	311	59
18	7.20	1750	200	88	424	10	648	572	295	86
19	7.55	1730	180	63	520	8	880	454	287	53
20	7.62	1380	104	82	222	9	340	235	290	39
21	7.65	590	337	33	137	10	36	335	329	22
Min	7.09	490	78	33	137	2	36	195	238	3
Mean	7.42	1460	177.5	75.2	378.9	9.36	512.4	419.8	292.7	36.7
Max	7.95	2640	358	146	638	13	1053	693	342	125
SD	0.26	538	77	31	142	3	323	155	27	33
Cv	3	37	42	39	35	27	60	35	9	90

Min minimum, *Mean* average, *Max* maximum, *SD* standard deviation, *Cv* variation coefficient

well number 9 in the center plain with a concentration of over 125 mg/l; the lowest value was recorded in well number 1 in the northwest boundary with a concentration of about 3 mg/l. The chemical analysis showed that nearly 57 % of water points have values higher than 50 mg/l, therefore higher than the desirable limit of NO_3^- for drinking water (50 mg/l) (OGRA 2011). The nitrate concentration in wells increases from the boundaries to the center of the area, where rural population is concentrated.

Classification of the water

The different water samples have been classified according to their chemical composition using the piper diagram. These diagrams are drawn by plotting the proportions in equivalents of the major cations on one triangular diagram, the proportions of the major anions on another, and combining the information from the two triangles on a quadrilateral. The position of this plotting indicates the relative composition of groundwater in terms of the cation–anion pairs that correspond to four vertices of the field (Thilagavathi et al. 2012). The postponement of the test results on physicochemical piper's digraph (Fig. 2) shows the existence of two major water types:
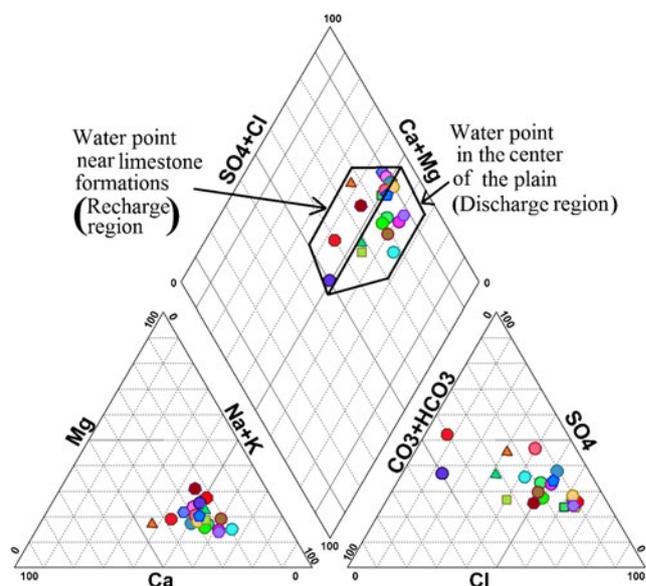

Fig. 2 Piper diagram applied to water of Ain Djacer aquifer

Ca-SO₄ and Cl-Na. The calcium sulfate water type is with low salinity concentrations but the chloride sodium water type is with high salinity concentrations. The first water type is located to limestone formations, and the second water type is located to the center of the plain. It is known that the chemical composition of water varies in time and space due to changes in recharge composition and flow patterns and due to chemical processes between the water and the porous environment. The common source of calcium in the groundwater is limestone in the sedimentary rocks. The chloride ion is widely distributed in natural water. Most Cl in the groundwater is from three sources including ancient seawater entrapped in sediment, solution of halite, and related minerals in evaporate deposits in the region (Belkhiri et al. 2010). Further addition of sulfate to the groundwater comes from the breakdown of organic matters in the soil and from addition of leachable sulfates in fertilizers of the intensively cultivated areas in Ain Djacer plain. Presence of fractured and karstified limestone formations on the east, west, and south boundaries suggests infiltration of rainfall (recharge region) where they acquired calcic facies which explains the presence of low salinity (TDS <1000 mg/l) of water on the east, west, and south boundaries. These waters mineralize advantage with chloride, sodium, and sulfate in contact with the Triassic salt formations and terrigenous formations forming the aquifer, by dissolving the salt and mineral by concentration in water of chemical elements along groundwater flow which explains the presence of high salinity (TDS > 1000 mg/l) of water on the center plain (discharge region).

Statistical analysis

Correlation analysis

The Pearson correlation coefficient matrix for Ain Djacer area is given in the Table 2. pH shows significant negative moderate correlation with carbonates elements (HCO_3^-, Ca^{2+}, and

Mg^{2+}). This is in liaison with the calc-carbonic equilibrium where the pH influences the dissolution of carbonate rocks. Salinity represented by the TDS shows a good correlation (0.53 to 0.98) with all elements except the nitrates. This indicates that these elements are the main component of salinity (Olive 1976). A strong positive correlation is observed between Mg^{2+} and Ca^{2+} with indication that most of the ions are involved in various physiochemical reactions, such as oxidation–reduction and ion exchange in the groundwater aquifer system (Udayalaxmi et al. 2010). This analysis also shows a moderate to strong correlation between SO_4^{2-}, Cl^-, Ca^{2+}, Mg^{2+}, Na^+, and K^+. This is attributed to the effect of leaching and dissolution of soluble salts of Trias (Freeze and Cherry 1979). This dissolution is verified by the stability indices. Thus, the negative saturation indexes, which indicate an under-saturation state of groundwater with respect to the halite, gypsum, and anhydrite. On the contrary, all groups of main mineral carbonates (calcite, aragonite, and dolomite) are super-saturated. Table 3. This is in association with the equilibrium constant (K) of the evaporate minerals (NaCl (1.58) CaSO₄ (−4.58)), which have higher values of K which allows them to present in water at high concentrations. The NO_3^- shows a moderate correlation with SO_4^{2-} (0.596), Cl^- (0.529), and K^+ (0.504) indicating that agricultural practices are significant in the study area.

Principal component analysis

The analytical results of principal component analysis were performed for the set of 21 samples and ten variables. Table 4 shows the eigenvalues of the extracted factors and the proportion of total sample variance explained by the factors. The analysis generates ten factors, and only two factors are significant which represent 65.1 % of total variance. Results from PCA are more efficient when the number of factors is small (Kraiem et al. 2014). The parameter loading for the two components from the PCA of the data set is given in Table 4. TDS,

Table 2 Pearson coefficients correlation for physicochemical parameters at the 0.05 level

	pH	TDS	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	Ca^{2+}	Mg^{2+}	Na^+	K^+
pH	1									
TDS	−0.009	1								
HCO_3^-	**−0.530**	**0.952**	1							
SO_4^{2-}	−0.011	**0.834**	−0.031	1						
Cl^-	0.250	**0.622**	0.333	**0.644**	1					
NO_3^-	−0.060	−0.435	−0.209	**0.596**	**0.529**	1				
Ca^{2+}	**−0.658**	**0.597**	**0.722**	**0.644**	**0.853**	−0.390	1			
Mg^{2+}	**−0.700**	**0.634**	**0.601**	**0.814**	**0.620**	−0.243	**0.684**	1		
Na^+	0.254	**0.931**	**0.714**	**0.714**	**0.787**	−0.428	**0.887**	0.426	1	
K^+	0.237	**0.514**	**0.597**	**0.618**	**0.813**	**0.504**	**0.857**	0.352	**0.919**	1

The bold values indicate the correlated variables

Table 3 Thermodynamic speciation (saturation indices of some minerals and the partial pressure of CO$_2$) calculations using PHREEQ-C

No. of wells	Anhydrite	Gypsum	Halite	Calcite	Aragonite	Dolomite	Log (P_{CO2})
1	−1.02	−0.8	−5.97	0.84	0.69	1.5	−2.46
2	−1.4	−1.18	−5.38	0.48	0.34	1.15	−2.23
3	−1.03	−0.81	−4.91	0.75	0.69	1.48	−2.44
4	−0.93	−0.7	−4.8	0.62	0.47	1.19	−1.94
5	−1.03	−0.81	−5.03	0.48	0.33	1.01	−2.07
6	−1.33	−1.11	−5.47	−0.22	−0.11	0.08	−1.73
7	−1.19	−0.97	−5.43	0.06	−0.09	−0.59	−1.51
8	−1.73	−1.49	−6.65	0.03	−0.37	0.19	−1.69
9	−0.97	−0.7	−5.16	0.25	0.1	0.35	−1.9
10	−0.93	−0.7	−5.37	0.56	0.42	1.09	−2.22
11	−1.3	−1.08	−5.47	0.61	0.46	1.09	−2.21
12	−0.97	−0.75	−5.01	0.69	0.55	1.29	−2.27
13	−1.13	−0.91	−5.21	0.22	0.08	0.36	−1.85
14	−1.36	−1.15	−5.42	0.55	0.41	1.19	−2.21
15	−1.47	−1.25	−6	0.15	0.1	0.38	−1.85
16	−1.53	−1.31	−5.83	0.83	0.68	1.46	−2.7
17	−1.03	−0.81	−5.22	0.38	0.24	0.75	−1.95
18	−1.15	−0.93	−5	0.24	0.09	0.36	−1.86
19	−1.55	−1.33	−5.75	0.29	0.15	0.83	−2.04
20	−1.31	−1.09	−7.09	0.54	0.39	0.9	−2.13
21	−1.33	−1.11	−5.65	0.42	0.27	0.72	−2.09
Min	−1.73	−1.49	−7.09	−0.22	−0.37	−0.59	−2.7
Mean	−1.34	−1.1	−5.59	0.24	0.22	0.62	−2.08
Max	−0.93	−0.7	−4.8	0.84	0.69	1.5	−1.51
Cv (%)	−24	−31	−12	36	42	41	−23

SO4, Cl, Ca, Mg, and Na marked factor 1, which explained 49 % of the variance. Factor 1 had a strong to moderate positive loading in TDS, SO4, Cl, Ca, Mg, and Na which were

Table 4 Variance explained and component matrixes

| Variable	Factor 1	Factor 2
pH	0.073	**−0.902**
TDS	**0.735**	0.256
HCO$_3$	0.242	**−0.934**
SO$_4$	**0.632**	0.323
Cl	**0.787**	0.007
NO$_3$	0.380	**0.600**
Ca	**0.822**	0.001
Mg	**0.744**	0.165
Na	**0.773**	0.093
Eigenvalue	4.89	1.60
Variance (%)	49.0	16.1
Cumulative (%)	49.0	65.1

The bold values indicate the correlated variables

0.735, 0.632, 0.787, 0.822, 0.744, and 0.773, respectively. High positive loadings indicated strong linear correlation between the factor and parameters. Thus, factor 1 can be termed as salinization factor. The TDS is positively correlated with the concentration of ions, which can thus be indirectly calculated from TDS. The aquifer consisted by evaporates could be supplied Na$^+$ and K$^+$, with the high value of Na$^+$ and K$^+$, whereas the limestone, dolomite, and calcareous concretions may provide the Mg^{2+} and Ca^{2+}. All these ions have high absolute values; what combined with more than 49 % variance could be explained by the factor 1, revealing that the factor 1 is the major factor for the ions form of groundwater samples. This axis reflects the role of natural factors such as dissolution of some carbonate, dolomitic, and evaporite minerals in the aquifer. Factor 2 explains 9.5 % of the total variance of the dataset and shows a significant bipolar characteristic. It has strong positive loadings on NO$_3^-$ (0.600), and the negative pole has a strong loading on pH (0.902) and HCO$_3^-$ (−0.934). The opposite evolution of HCO$_3^-$ and NO$_3^-$ could be explained by the carbonate weathering and could reflect the influence of acid–base equilibrium conditions on groundwater chemistry (Kraiem et al. 2014). Factor 2 is mostly associated

with chemical fertilizers. Large amounts of fertilizer, such as urea and commercial composite, have been applied for long times which are a major constituent resulting from the return flow from development of irrigation. Under oxic conditions, the main component of fertilizers, NH_4^+, is easily oxidized to NO_3^- by the nitrification process according by the reaction (2) to (Kim et al. 2003).

$$NH_4^+ + 2O_2 \rightarrow NO_3 + H_2O + 2H^+ \qquad (2)$$

This process allows the acidification of the environment following the release of H^+ ions in the groundwater. Furthermore, the concentration of HCO_3 in the groundwater probably is associated to infiltrating water that has incorporated dissolved CO_2 from root respiration and decay of soil organic matter. This is a constituent which results from the dissolution of CO_2 in the water and posterior dissociation of the H_2CO_3 according by the reaction (3) formed by (Ruiz et al. 1990).

$$H_2CO_3 + H_2O \rightarrow HCO_3^- + H_3O^+ \qquad (3)$$
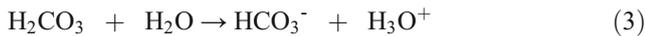
The association of these two parameters reflects the influence of using fertilizers on pollution of groundwater and can thus be termed as the agriculture contamination factor (Zghibi et al. 2014).

Cluster analysis

Two different methods can be applied to identify clusters, including R- or Q-modes (Dalton and Upschurch 1978). R-mode is usually applied to water quality variables to reveal the interactions between them, while Q-mode reveals the interactions between the studied samples. Nine hydrochemically measured variables (TDS, Ca, Mg, Na, K, Cl, SO4, HCO3, and NO3) were utilized in this analysis. For statistical purpose, all the variables were log-transformed and more closely corresponded to normally distributed data. Subsequently, they were standardized to their standard scores (z-scores) as described by Güler et al. (2002). As there is no test to determine

Table 5 Mean parameter values of the three principal water groups (determined from HCA)

Group		G1	G2	G3
TDS	(mg/l)	816.4	1492.6	2638.7
Ca^{2+}	(meq/l)	**5.0**	8.2	**12.3**
Mg^{2+}	(meq/l)	4.5	4.8	7.7
Na^+	(meq/l)	3.0	**11.8**	**14.9**
K^+	(meq/l)	0.1	0.1	0.2
HCO_3^-	(meq/l)	**6.0**	4.7	5.0
SO_4^{2-}	(meq/l)	4.0	7.0	**11.4**
Cl^-	(meq/l)	4.5	**11.7**	**27.4**
NO_3^-	(meq/l)	0.3	0.5	0.2
% wells		24	62	14

The bold values indicate the dominant elements

the optimum number of groups in the dataset (Güler et al. 2002), the visual inspection is the only criteria to select the groups in the dendrogram (Fig. 3). The defined phenon line (Sneath and Sokal 1973) was chosen at a linkage distance of 250. At this distance, the groups could be distinguished in terms of their hydrochemical variables. As shown in Fig. (3), nine variables were classified into three groups of groundwater. The G1 with low salinity (TDS < 1000 mg/l), G3 with high salinity (TDS > 2000 mg/l), and G2 with intermediate and average salinity (1000 < TDS < 2000 mg/l). The first group is composed of the wells 1, 4, 8, 15, and 21, influenced only by the carbonate facies outcrops, and it is characterized by Ca and HCO3. Table 5. It is located near the outcrops east and west. For the group 3, it is located in the center and the north of the plain where there is a convergence of flows. This group is composed of the wells 7, 9, and 16. It is influenced by the outcropping Triassic saliferous located in the northland and characterized by Na-Ca and Cl-SO4. A local contamination by septic tanks, sewage systems, agricultural fertilizers, and dissolution of the formations clay, marl, and salt and could be responsible for this elevation as it has been shown by Belkhiri et al. (2010) in other regions of the country. Group 2 is a term of transition between the two extreme

Fig. 3 Dendrogram of cluster analysis of variables and the hydrochemical samples
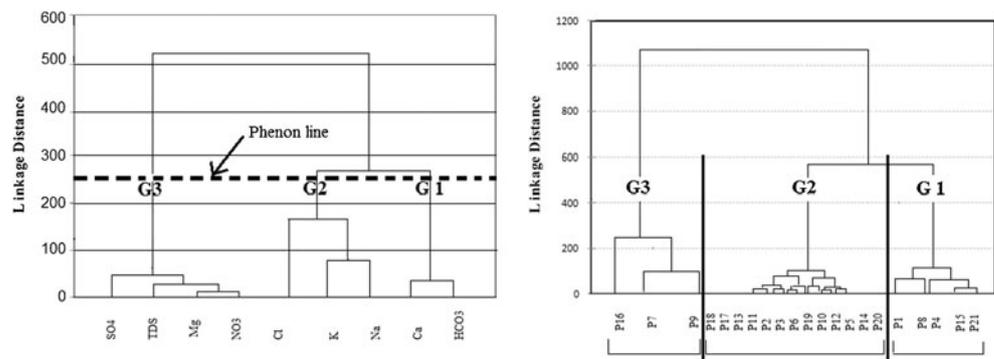
groups, and it is composed of the wells 2, 3, 5, 6, 10, 11, 12, 13, 14, 17, 18, 19, and 20, and it is characterized by Na and Cl. Figure 1. This logic of succession (G1-G2-G3) is in agreement with the flow that allows the concentration of elements in the rows and lines of underground flow.

Conclusion

This study is contributed to the knowledge of hydrochemical functioning of the superficial aquifer of Ain Djacer using multivariate statistical techniques including principal component analysis and cluster. These techniques can successfully be used to derive information from the data set about the possible influences of the environment on groundwater quality and also identify natural groupings in the set of data. The water of this aquifer has a carbonate facies on calcareous limits near the infiltration area. The salt water is concentrated in gypsiferous elements along the flow lead to a final facies type Na-Cl. Three major water types are suggested by the Q-mode HCA analysis according to salinity increasing according to the direction of flow. The presence of NO_3^- in groundwater is mainly related to agricultural activity.

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