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Research Article Water Quality Assessment for Drinking and Irrigation using Major Ions Chemistry in the Semiarid Region: Case of Djacer Spring, Algeria

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Abstract

Objective: Variation of major ions chemistry was used to evaluate the geochemical processes of groundwater in the shallow aquifer of Djacer spring located in the Quaternary alluvial formations, eastern Algeria. **Methodology:** Diagrams such as Piper diagram, Gibbs diagram, Durov and Wilcox diagram as well as the hardness, soluble sodium percentage and the permeability index all have been used to assess the diagram quality of the groundwater of Ain Djacer spring aquifer. The statistical tests such as mean, median, standard deviation, kurtosis and skewness were used to test the homogeneity of the initial data. **Results:** These methods highlighted two water groups, where salinity increases with flow direction and the total dissolved solids is as a major distinguishing factor in these groups. High rates are due to the ion exchange and water-rock interaction processes dominated by dissolutions, evaporation and precipitation with the presence of saliferous formations. Piper diagram and Durov diagram showed that the water type was calcium bicarbonate in the boundaries and evolved to sodium chloride in the center of the plain. Therefore, the hydrochemical and the stability index showed that groundwater salinity is much more controlled by saliferous minerals in contact with terrigenous salt formation and carbonate minerals. **Conclusion:** Water quality for irrigation and domestic use is good near the boundaries but poor in the center of the plain because of its high salinity.

Key words: Groundwater, salinity, water rock interaction, irrigation, arid region, Djacer spring

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Data Availability: All relevant data are within the paper and its supporting information files.

INTRODUCTION

A clean and dependable supply of water is necessary to ensure a high quality of life, a strong economy and a strong agricultural development. In typical arid and semiarid areas, groundwater is the major source of water for most uses¹. Intensive cultivating and urban development has caused a high demand on groundwater resources in these regions around the world² and in Algeria. It is estimated that approximately two-third of the water is used for irrigation³. The evaluation and management of this water resources require an understanding of hydrogeological and hydrogeochemical properties of those aquifers⁴. A large number of groundwater studies also have focused specifically on the assessments of its suitability for irrigation purposes as investigated by Subramani *et al.*⁵, Haritash *et al.*⁶ and Hosseinifard and Aminiyan⁷.

The groundwater chemistry is an essential parameter for evaluating potential exploitable water of an aguifer⁸. The main factors influencing hydrochemical groundwater guality are precipitation and dissolution of minerals, ion-exchange and sorption and desorption in the groundwater flow⁹. This situation is compounded by the complexity of the mineralogy saliferous, over exploitation of the aquifer and its low recharge, which limits the usable capacity of the aquifer this because of the considerable variation in the concentration of ions and the Total Dissolved Solids (TDS)¹⁰. At the same time, the environmental impacts of human activity like unused fertilizers, pesticides, sewage water and discharge of industrial effluents are considered as potential anthropogenic sources responsible for contamination of the groundwater¹¹. The presence of different chemical and physical constituents in excess of their permit limits for various uses can create health hazards and environmental problems¹² and hence the water quality analysis is critical in ensuring that water consumed by the population meets the required guality standards¹³. This situation can be modeled by graphical and geochemical models and these techniques are commonly used to reconstruct geochemical evolution of groundwater in the direction along the groundwater flow path. Several studies have been undertaken to determine the hydrochemical processes and factors that influence the chemistry of shallow groundwater. Recently, Kura et al.14 used graphical and geochemical models to characterize and determine a spatiotemporal variation in groundwater of groundwater along the flow path in India. Ghodbane et al.¹⁵ used statistical techniques to evaluate the variations of groundwater hydrochemistry in Algeria. Belkhiri et al.¹⁶ used multivariate statistics and inverse geochemical modelling to assess and

characterize the groundwater flow of Azel spring in Algeria, Chang and Wang¹⁷ used major ions chemistry of groundwater in northwestern China to assess hydrogeochemistry in arid area, Reddy *et al.*¹⁸ determined the hydrochemical processes and factors of contamination of groundwater in Patancheru industrial area, Southern. Desa *et al.*¹⁹ used modelling techniques to assess the usability of the Gulf of Kachchh waters based on spatial and temporal variations in dissolved oxygen as a pollution indicator.

In North-East Algeria, the agricultural plain of Djacer spring is irrigated from the shallow alluvial aquifers, comprises fluvial sediments of the Miocene-Pliocene-Quaternary age. In study area, agriculture is the most important economic activity affecting the changes in groundwater guality by anthropogenic activity. During the last decade or so, the region has known a rough drought and the absence of surface water, resulted an increasing dependence on groundwater sources. The over-exploitation of the aquifer yielded progressive deterioration of the water quality in the irrigated area with the appearance of areas of high salinity (TDS>2 g L^{-1}) which create problems of water use. In light of these trends, there is an urgent need to better understand the inter-connectivity of the shallow alluvial aguifers with underlying (salty) formations and to constrain the exploitation of this water resource³.

Thus main objectives of the present study were (1) To determine the groundwater quality, (2) To identify the major hydrogeochemical processes and (3) To delineate regions where groundwater is suitable or unsuitable for drinking and irrigation on the basis of data from 21 groundwater samples, taken during March, 2013.

MATERIALS AND METHODS

Study area: The Djacer spring basin is located in the North-Eastern part of Algeria, centered on latitude 35°49'50" N and longitude 6°00'16" E. The locations of the sampling points are shown on the map (Fig. 1). The flat morphological nature of the basin resulted in the observed weak hydrographic endorheic network, drained mainly by the Gadaine salt lake (Chott) during heavy rains. The region's climate was of a semi-arid type, characterized by an average yearly rainfall of around 360 mm while the average yearly temperature is 13°C²⁰. This semi-arid climate often results in water shortages.

The geological setting of the study area is mainly constituted by Triassic and Cretaceous rocks overlain by recent quaternary deposits. Triassic evaporites diapirs are found in the Northern part of the study area. This latter unit is composed highly deformed limestone and dolomite along Asian J. Earth Sci., 10 (1): 9-21, 2017



Fig. 1: Map of naturals conditions showing lithology, salinity and sampling sites

with a clay matrix of kaolinite, illite, smectite and as well as gypsum and halite. Conglomerates are also not uncommon. Cretaceous formations are mainly limestone and sandstone, sometimes with thick layers of marl, the lower parts are dolomites. The cover formations are mainly quaternary. They correspond to red clay, sometimes gypsum, conglomerates and alluvium²¹. The thickness of this formation varies between 300 and 500 m²².

The hydrogeological investigation carried out in this area highlighted the existence of a shallow aquifer, located in the quaternary alluvial formation laying on clays, marls and sometimes gypsum²³, with a thickness of about 10-100 m in the center of the plain. These alluvial deposits have an average permeability²³ of 10^{-4} m sec⁻¹. The aquifer maintained the same structure, characterized by the presence of two zones, the first, in the West with a West-East flow path and the second to the East with an East-West flow. These flow directions are imposed by the geometry of the substratum. These two flow paths converge towards the center of the plain before they get drained to the North. This potentiometric configuration (Fig. 1) suggests a recharge from the fractured Cretaceous limestone formations surrounding Djacer spring depression.

Sampling and analysis: During March, 2013, 21 groundwater samples were collected from the study area (Fig. 1). These samples were taken from drinking water wells after 15 min of pumping, sufficient time enough for water temperature to stabilize and become representative of the temperature of the aquifer. The pH, the electrical conductivity (μ S cm⁻¹ at 25 °C) and the Total Dissolved Solids (TDS) were measured in the field using a WTW multiparameter (P3 MultiLine pH/LFSET)

and TDS-meter, respectively. Subsequently, the samples were analysed in the laboratory for their chemical constituents such as calcium (Ca²⁺), magnesium (Mg²⁺), sodium (Na⁺), potassium (K⁺), chloride (Cl⁻), bicarbonate (HCO₃⁻), sulphate (SO₄²⁻) and nitrates (NO₃⁻). This was achieved using standard methods as suggested by the American Public Health Association²⁴. The accuracy of the chemical analysis was verified by calculating the ion-balance, the errors were generally around 5%.

Methods for hydrochemical evaluation: This study provides a detailed geochemical characterization using chemical data from 21 groundwater samples, taken from the superficial aquifer. This typological analysis was done using various molar ratios of chemical elements and graphical tool to replenish hydrochemical process thereto. This work tries to make a spatial assessment of Djacer spring hydrochemistry.

Hydrogeochemical regime was evaluated with classic geochemical techniques, the definition of major ion molar ratios and the graphical interpretation through Piper²⁵ diagram, Durov²⁶ diagram and Gibbs²⁷ diagram. AqAQ RockWare 1.5 demo Free Software package was used to plot the Piper, Gibbs and Durov diagram's. Raw analytical data results were combined with geological and hydrogeological information to provide an insight to groundwater chemical composition and evolution. That was supplemented by the use of hydrogeochemical molar ratios (meg L⁻¹) which are widely used for the evaluation of geochemical processes that govern groundwater evolution and the relative importance of ion exchange. For this, different molar ratios and Chloro-Alkaline Indices (CAI) have been used. It is essential to know the changes in chemical composition of groundwater during its travel in the sub-surface²⁸. The Chloro-alkaline indices [CAI = {Cl-(Na+K)}/Cl] as suggested by Schoeller²⁹ indicates the ion exchange between the groundwater and its host rocks. This analysis will be completed using the calculation of the Saturation Index (SI) of some evaporates minerals and carbonates using PHREEQC hydrogeochemical modeling software³⁰. The suitability of the water for drinking and irrigation has been studied with diagrams such as: Piper, Gibbs, Durov, Wilcox³¹, total hardness³², soluble sodium percentage³² and the permeability index³³.

Table 1: Statistical summary of hydrogeochemical parameters

Statistical analysis: The homogeneity of the data is verified using a few tests such as mean, median, Standard Deviation (SD), kurtosis (Kurt) and skewness (Skew). Mean and median explains average value and standard deviation gives a measure of variability of the sample³⁴. Kurtosis and skewness are used for verifying whether the distribution of a sample is normal³⁴. It is considered that the sample follows a normal distribution to 95% when the value of kurtosis and skewness between -2 and +2 and the value of the skewness between -2 and +2³⁴. All mathematical and statistical computations were made using MS Excel Professional Plus 2010³⁵.

RESULTS

Statistics of the chemical compositions of the groundwater samples are shown in Table 1. The examination of this table shows that all the median values are substantially equal or near to the average value except those of nitrates and all variables have values of kurtosis and skewness which are close to 1. Examination of values of the pH, are indicating low alkalinity in the groundwater. The pH of groundwater in the study area is within the limits (6.5-9.5) of WHO guideline³⁶ for drinking water quality. The electrical conductivity of the water samples are under test were rated in the category permissible to unsuitable (EC = 1,500-3,500 μ S cm⁻¹) for irrigation purposes³⁴. Except for two samples which are within moderate class, all other samples are higher than desirable limit $(2000 \,\mu\text{S cm}^{-1})$ of WHO guideline³⁶ for drinking water guality. Salinity represented by the TDS, varies between 918 and 2,493 mg L⁻¹. The FAO standard range of TDS value for irrigation practices³⁵ is 450-2,000 mg L⁻¹. Salinity represented by the TDS shows 23% of samples of values are higher than the prescribed limit. Higher concentrations indicate that the ionic concentrations are more in the groundwater. The highest concentrations are in the center of the plain while the lower concentrations are near the carbonate formations at the boundaries. This distribution suggests the existence of two areas with progressive salinity, from the boundaries (West, East and South) to the center (Fig. 1).

Tuble 1. Statistical sammary of Hydrogeoenemical parameters												
		TDS	EC	TH	Ca ²⁺	Mg ²⁺	Na ⁺	K+	CI-	SO4 ²⁻	HCO ₃ -	NO_3^{-}
Parameters	рН	(mg L ⁻¹)	(µS cm ⁻¹)	$(mg L^{-1})$	(mg L ⁻¹)	$(mg L^{-1})$	$(mg L^{-1})$					
Min	7.00	918.0	1434.0	41.0	104.0	33.0	128.0	2.0	136.0	180.0	187.0	3.0
Mean	7.50	1567.0	2448.0	77.6	227.5	75.2	292.1	8.5	350.4	329.4	345.2	36.7
Median	7.55	1554.0	2419.0	66.0	224.0	73.0	283.1	9.0	332.0	385.0	327.2	23.0
Max	8.20	2439.0	3811.0	149.0	428.0	146.0	520.0	12.0	880.0	671.0	587.0	125.0
SD	0.28	423.8	662.2	28.8	90.3	29.9	125.8	2.6	213.6	138.6	116.7	32.2
Kurt	0.62	-0.4	-0.4	1.0	-0.7	0.7	-1.3	1.7	0.1	0.1	-1.0	0.8
Skew	0.02	0.5	0.5	0.5	0.4	1.1	0.4	-1.5	1.1	0.9	0.3	1.1

TDS: Total dissolved solids, EC: Electrical conductivity, TH: Hydrotimetric title, Min: Minimum, Max: Maximum

The content of Ca²⁺ in water samples collected from different sites of Djacer spring area varied from 104-428 mg L⁻¹. Irrigation waters containing less than 20 meg L⁻¹ (400 mg L⁻¹) Ca²⁺ is suitable for irrigating crops³⁴. Considering this value as standard, Ca²⁺ content in 95% water samples could safely be used for irrigation and would not affect soils. All the samples analyzed exceed the desirable limit (75 mg L^{-1}) of Ca²⁺ of WHO guideline³⁶ for drinking water. The concentration of Mg²⁺ in water samples is within the range of 33-146 mg L^{-1} . Irrigation waters containing less than 5 meq L^{-1} (60 mg L^{-1}) Mg²⁺ is suitable for irrigating crops³⁴ and 62% of water samples are above this limit and may have a negative impact on soils. Seventy-five percent of samples exceed the desirable limit (50 mg L⁻¹) of Mg²⁺ of WHO guideline³⁶ for drinking water. The concentration of Na+in water samples of spring area varied from 128-520 mg L^{-1} . Irrigation water generally containing less than 40 meq L⁻¹ (920 mg L⁻¹) Na+is suitable for crops and soils³⁴. The observed Na content in all water samples had far below this specified limit. The concentration of K+present in the water samples ranged from 2-12 mg L⁻¹. The recommended limit of K+in irrigation water³⁴ is 2.0 mg L⁻¹. Considering this value as standard, the waters of the Djacer spring area could problematic for long-term irrigation. Bicarbonates are derived mainly from the soil zone CO₂, dissolution of carbonates and reaction of silicates with carbonic acid³⁴. The concentration of HCO₃⁻ in water samples were within the range of 187-587 mg L⁻¹. In respect of HCO₃⁻⁻ content, all water samples were found suitable for irrigation, which exceeded the permissible limit (610 mg L⁻¹)³⁴. The sodium (Na⁺), potassium (K^+) and bicarbonate (HCO_3^-) does not have any prescribed limit for drinking water guality, but high concentration of sodium ion results in salty nature of water. Water samples collected from Djacer spring area contained a chloride concentration (Cl⁻) ranging from 136-880 mg L⁻¹. Maximum permissible limit of Cl⁻ in irrigation water is 30 meg L⁻¹ $(1064 \text{ mg } \text{L}^{-1})^{34}$ and all samples collected from Djacer spring area were within the permissible limit. Eighty percent of samples exceed the desirable limit (200 mg L⁻¹) of chloride (Cl⁻) according to WHO guideline³⁶ for drinking water. The SO₄²⁻ content in water samples under study ranged from 180-671 mg L⁻¹. The maximum permissible limit of SO₄²⁻ in irrigation water is 20.00 meg L^{-1} (960 mg L^{-1})³⁴ and all water samples collected from Djacer spring area are below this acceptable limit of irrigation water quality. Only ten percent of samples exceed the desirable limit (500 mg L⁻¹) of sulphate (SO₄²⁻) of WHO guideline³⁶ for drinking water. The NO₃⁻ content in water samples collected from Djacer spring area varied from 3-128 mg L⁻¹. The permissible limit of nitrate for irrigation water³⁵ is 10 mg L⁻¹ and considering this limit as

standard, the NO₃⁻ values in 67% of water samples were above permissible limit for irrigation that might be harmful for crop production. Examination of the values of nitrate concentrations shows that only 28% of the samples exceeded the desirable limit of NO₃⁻ (50 mg L⁻¹) of the WHO guideline³⁶.

The hydrochemical facies reflect the effect of chemical processes in the lithological environment and the contained groundwater flow patterns³. In this study, we used to Piper and Durov diagrams to determine the hydrochemical facies of groundwater. Examination of the molar concentrations of different elements in the plain boundary shows that the cations evolve as follow: $Ca^{2+}>Mg^{2+}>Na^+>K+$ while the anions evolve in the following manner: $HCO_3^{-}>CI^{-}>SO_4^{2-}$ in 53% of cases. The mean concentration of Ca^{2+} is recorded with 227.5 mg L⁻¹ for HCO_3^{-} with 345.2 mg L⁻¹. While in the center of the plain the examination of the molar concentrations of different elements shows that the cation concentrations of the follow: $Na^+>Ca^{2+}>Mg^{2+}>K+$ while the anions move to the following manner: $CI^->SO_4^{2-}$ in 47% of cases.

The geochemical evolution of groundwater can be understood by plotting the milliequivalent (meq L⁻¹) concentrations of major cations and anions in the Piper trilinear diagram. The diamond plot (Fig. 2) can further be divided into five zones (A, B, C, D, E and F) in order to distinguish different types of groundwater. In zones A, B, C and D, two groups of anions and cations are dominant. It is further evident from Fig. 2 that most of the groundwater samples (57%) are in zone E (mixed zone) and (43%) are in zone C.

The Durov diagram was employed in order to understand the hydrochemical process controlling the groundwater system. This diagram (Fig. 3) shows that the water from carbonated limits is positioned in the box 1. It characterizes a water rich in Ca-HCO₃, thus recharging¹⁰. The water from the center of the plain, is positioned in the box 3 rich in Na-Cl, resulting ion exchange (Ca-Na) and a dissolution of evaporate minerals¹⁰. This confirms the interaction of water with the rock.

The Total Hardness (TH) of the groundwater is mainly driven by elevated Ca^{2+} and Mg^{2+} concentrations released from the calcite and dolomite buffering process. Hardness (mg equivalent $CaCO_3 L^{-1}$) can be determined by substituting the concentration of calcium and magnesium, expressed in mg L^{-1} , by the Eq. 1³²:

According to the criteria described by Haritash *et al.*⁶, out of 21 water samples, 90% of the samples collected during the monitoring period are characterized by soft to moderately hard conditions (total hardness as $CaCO_3 < 120 \text{ mg L}^{-1}$).

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Fig. 2: Piper's diagram of groundwater in the area



Fig. 3: Durov's diagram of groundwater in the area

Sodium content is the most troublesome of the major constituents and an important factor in irrigation water quality evaluation. Excessive sodium leads to development of an alkaline soil that can cause soil physical problems and reducing soil permeability⁷. Furthermore, irrigation water containing large amounts of sodium is of special concern due to absorbed sodium by plant roots which is transported to leaves where it can accumulate and cause injury⁷. However,

there is a restriction in use of overhead sprinklers method with water contained a high level of sodium salts because these salts can be absorbed directly by plant leaves and will produce harmful effects. The Soluble Sodium Percentage (SSP) is an important parameter for determining the suitability of groundwater for irrigation because it is a measure of alkali/sodium hazard to crops. The SSP is defined by the Eq. 2³³:

$$SSP = \frac{Na^{+}}{Ca^{2+} + Mg^{2+} + Na^{+} + K^{+}} \times 100$$
 (2)

where, all the ions are expressed in meq L^{-1} .

The SSP with the EC are used to establish the Wilcox diagram. Water with SSP greater than 60% may result in sodium accumulations that will cause a decrease of the soil's physical properties³³.

DISCUSSION

The examination of the Table 1 of the statistics summary of hydrogeochemical parameters shows that the samples are homogeneous. This is confirmed by the values of average, median, Kurt and Skew. The low value of the standard deviation indicates that the data points tend to be close to the mean of the set. These might values of the pH be due to the presence of higher amount of ions such as Ca, Mg and Na in water³⁷. According to proposed Food and Agriculture Organization of the United Nations (FAO), the acceptable range of pH for irrigation water is 6.5-8.5³⁸ and there are no water samples with pH values outside of the desirable ranges. The Higher electrical conductivity and the TDS value of the water samples reflected the higher amount of salt concentration which affected irrigation water guality related to salinity hazard³⁹. The FAO standard range of TDS value for irrigation practices⁴⁰ is 450-2,000 mg L⁻¹. About 23% of samples show values higher than the prescribed limit. Higher concentrations indicate that the ionic concentrations are more in the groundwater. The highest concentrations are in the center of the plain while the lower concentrations are near the carbonate formations at the boundaries. This distribution (Fig. 1) suggests the existence of two areas with progressive salinity, from the boundaries (West, East and South) to the center. This salinity changes from a less salty group in the West and East (TDS <1,500 mg L^{-1}) reflecting recharge⁴¹ to a second group of high salinity (TDS>1,500 mg L^{-1}) in the center. The Djacer spring plain is an area where a flow is a relatively small change in topography; 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, leaching and dissolution processes from the aquifer matrix. So this zonation appears to be controlled by two factors, first, groundwater flow and the second, geology. These large variations contrast with the quasi stability of pH. This implies that despite concentration of solution by evaporation and transpiration, carbonate precipitation regulates pH. According to Belkhiri and Mouni⁴¹ and Lecinaa *et al.*⁴², the residual alkalinity concept solutions evolve in the neutral pathway and not in the alkaline one.

The contribution of Ca²⁺ content in water was largely dependent on the solubility⁴³ of CaCO₃ and CaSO₄. Irrigation waters containing less than 20 meq L^{-1} (400 mg L^{-1}) Ca²⁺ is suitable for irrigating crops³⁹ and 95% water samples could safely be used for irrigation and would not affect soils. The Irrigation waters containing less than 5 meg L^{-1} (60 mg L^{-1}) Mg²+is suitable for irrigating crops³⁹ and 62% of water samples are above this limit and may have a negative impact on soils. Sodium in the aquifer system is mainly derived from dissolution of salt minerals and silicate weathering⁴⁴. Irrigation water generally containing less than 40 meg L^{-1} (920 mg L^{-1}) Na+is suitable for crops and soils³⁹. The observed Na content in all water samples had far below this specified limit. The recommended limit of K+in irrigation water is 2.0 mg L^{-139} . Considering this value as standard, the waters of the Djacer spring area could problematic for long-term irrigation. Bicarbonates are derived mainly from the soil zone CO_{2} , dissolution of carbonates and reaction of silicates with carbonic acid⁴⁵. The concentration of HCO₃⁻ in water samples were found suitable for irrigation, which exceeded the permissible limit (610 mg L⁻¹)³⁹. The large lateral variations in the Cl⁻ concentrations in some sites indicate local recharge and are attributed to contamination by anthropogenic sources including agricultural runoff and leaching of saline residues in the soil⁴⁶. Maximum permissible limit of Cl⁻ in irrigation water is 30 meg L⁻¹ (1064 mg L⁻¹)³⁹ and all samples collected from Djacer spring area were within the permissible limit. The SO₄²⁻ in aguifer system are derived mainly from rock weathering include two major forms of sulphur sedimentary rocks, pyrite and gypsum⁴⁷. All water samples collected from Djacer spring area are below this acceptable limit of irrigation water quality in SO₄^{2–}. Examination of the values of nitrate concentrations shows that only 28% of the samples exceeded the desirable limit of NO_3^- (50 mg L⁻¹) of the WHO guideline³⁶. This is in liaison with the use of fertilizers (chemical and/or organic) and the decomposition of organic matter, as has been reported in other recent studies in Eastern of Algeria²².

The geochemical evolution of groundwater can be observed that during the groundwater flow, the groundwater tends to become Na-Cl type from Ca-HCO₃ type. The groundwater samples (57%) are in zone E (mixed zone) wherein groundwater types cannot be identified as neither anions nor cations dominant⁴⁸ and having with carbonate enrichment with an indication of groundwater from formations that are composed of limestone or from active recharge zones with short residence times⁴⁹. Samples plotting in zone C (43%) belong to the class illustrating halite dissolution (saline), salts deposited by evapotranspiration of irrigation water and reverse/inverse ion exchange⁵⁰ responsible for the controlling of the chemistry of the groundwater and subsequent mixing with groundwater.

The Durov diagram was employed in order to understand the hydrochemical process controlling the groundwater system. In general, the potential sources of Na, Cl and SO₄ ions in groundwater are the dissolution of halite, gypsum and related salty minerals, leaching of rocks and minerals from (upper) soil layer by weathering and erosion and anthropogenic activities⁵¹. The dominance of Ca²+and HCO₃⁻ on boundaries and Na⁺-Cl⁻ in the center of the plain, is in relationship with the geology and the groundwater flow. The boundaries of the plain are constituted by carbonates while the center of the plain is formed of clay and gypsum-marls belonging to the Quaternary age. The presence of fractured and karstified limestone in the plain boundary, suggests the infiltration of effective rainfall where they acquire the Ca²⁺-HCO₃⁻ facies⁵². These waters get mineralized more in Na⁺ and Cl⁻ in contact with terrigenous saline formations constituting the aquifer.

The evolution of the groundwater chemistry is conditioned by the water-rock interaction processes, depending largely on the chemistry of the water charging, of the lithology of the aguifer in which the water is stored and the water residence time. The evaluation of this process requires the knowledge of the mineralogy of the surrounding rock and the identification of the chemical reactions responsible for the geochemical evolution of these waters. Ziani et al.22 showed that lake sediments of Quaternary age in the region are rich in calcite, dolomite, quartz, montmorillonite, illite, smectite, chlorite, cristobalite, siderite, ankerite, albite, kaolinite and gibbsite. Generally, three processes contribute to the generation of solutes in groundwater: evaporation, dissolution of carbonates and evaporates and base exchange⁵³. These processes are examined using several diagrams and ion ratios. The salinity of these two groups can have two origins, either carbonates or saline formations.



Fig. 4(a-c): (a) Plot of TDS vs $(Ca+Mg+HCO_3)/Na+K+CI+SO_4)$, (b) Plot of TDS vs Na/(Na+Ca) and (c) Plot of TDS vs $CI/(CI+HCO_3)$

To demonstrate this phenomenon we have established a diagram (Fig. 4a) in which these elements are represented: $(Ca^{2+}+Mg^{2+}/Na^{+}+Cl^{-}+SO_4^{2-})$ vs TDS. The sampled points are grouped in two families. This is related to the equilibrium constants of these two groups of minerals, they are stronger evaporate [NaCl (1.58), CaSO₄ (-4.58)], which allows them to present themselves in water at high concentrations. By contrary to carbonate minerals, the equilibrium constant is lower [Dolomite (-17.02), Calcite (-8.37)], which produce a precipitation of these chemical elements⁵⁴. rapid Ahmed et al.55 also pointed out that the weathering rate evaporates and carbonates that are respectively 80 times and 12 times faster than that of silicates which explains the difference by which these two minerals affect the salinity. The calculation of Saturation Indices (SI) of the mineral phases using the program PHREEQC hydrogeochemical modeling

Table 21 bladsteal barmany of balandion malees of bonne minerals										
Parameters	Aragonite	Calcite	Dolomite	Gypsum	Anhydrite	Halite				
Minimum	-0.60	-0.46	-1.07	-1.32	-1.54	-6.67				
Average	-0.15	-0.01	-0.17	-1.00	-1.22	-5.77				
Median	-0.34	-0.20	-0.28	-0.99	-1.21	-5.92				
Maximum	0.33	0.47	0.57	-0.81	-1.03	-5.00				
Standard deviation	0.32	0.32	0.51	0.12	0.12	0.45				

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Table 2: Statistical summary of saturation indices of some minerals

software (Table 2) shows that the solution is undersaturated (-6.67 to -0.81) for the main evaporate minerals, reflecting a relatively long contact time with these minerals to allow dissolution. This suggests that their soluble component Na⁺, Cl^{-} , Ca^{2+} and SO_4^{2-} concentrations are not limited by mineral equilibrium and results in the formation of Ca-HCO₃ type groundwater¹⁶. The calculation of the SI of carbonate minerals shows that the solution is undersaturated for the samples situated close to the boundaries (42%) and is saturated (58%) for the samples situated in the center of the plain. Boundaries area is a zone of recharge where water precipitates through low strength minerals which allows dissolution of minerals. By against the water of the central plain are highly charged which allows precipitation of minerals. The values of the indices are smaller in the recharge area if compared with those in the downgradient area. Those isograms provide information on the recharge and resident time (water-minerals reaction time) of groundwater⁴¹. This process generally enriches the groundwater in rock forming elements such as Ca²⁺ and HCO3⁻ and results in the formation of Ca-HCO3 type groundwater. The hydrochemical type varies from the Ca-HCO₃ to the Cl-Na type, which shows that from the boundary to the plain center, the water quality is gradually deteriorating along the groundwater flow path. These values provide information on the recharge and resident time (water-minerals reaction time) of groundwater⁴¹.

The Gibbs plot (Fig. 4b, c) for the study area indicated that the ion composition is controlled by evaporation-crystallization close to the boundaries and by rock weathering in the center of the plain. This confirms that water–rock interaction is the mechanism responsible for the chemical composition of the groundwater. The Na⁺ and Cl⁻ are the dominant ions in the center of the plain while Ca²⁺ and HCO₃⁻ are the dominant ions in the boundaries. It is known that the dissolution of NaCl and CaSO₄, produces in the middle,1 mol of Na, 1 mol of Cl, 1 mol of Ca and 1 mol of SO₄. When represented on a diagram (Fig. 5a), these bonds result in straight slope of 1:1. The analyzed groundwater samples which have straight, slope different from 1:1 indicate an excess of Na.

The increase in ionic concentrations in the groundwater could also be estimated by the Chloro-Alkali Index (CAI). If there is ion exchange of Na and K from water with calcium in



Fig. 5(a-c): (a) Plot of Cl vs Na, (b) Plot of TDS vs CAI and (c) Plot of SO₄ vs Ca

the rock, the exchange is known as direct when the indices are positive. If there is ion exchange of Na⁺ and K⁺ from water with calcium in the rock, the exchange is known as direct when the indices are positive. If the exchange is reverse then the exchange is indirect and the indices are found to be negative. The CAI calculated for the waters of the study area (Fig. 5b) shows that the water samples for boundaries are found to be negative (TDS<1,500 mg L⁻¹ and CAI<-0.5). By against the CAI calculated for water samples for the central part of the plain are found to be superior (>-0.5) and have TDS>1,500 mg L⁻¹.



Fig. 6(a-b): (a) Plot of Ca vs HCO₃ and (b) Ca+Mg vs SO₄+HCO₃

The Ca²⁺ and SO₄²⁻ relationship (Fig. 5c) shows an excess in Ca²⁺ for water with low salinity (TDS <1,500 mg L⁻¹) and an excess in SO₄²⁻ for water with high salinity (TDS>1500 mg L⁻¹). The presence of Na⁺, Cl⁻ and SO₄²⁻ is due to dissolution of the evaporite minerals such as Halite, gypsum, anhydrite and epsomite according to the Eq. 3-5:

$$NaCl \rightarrow N^{+}+Cl^{-}$$
 (3)

$$CaSO_4, 2H_2O \rightarrow Ca^{2+} + SO_4^{2-} + 2H_2O$$
(4)

$$MgSO_{4}, 7H_{2}O \rightarrow Mg^{2+} + SO_{4}^{2-} + 7H_{2}O$$
 (5)

The Ca²⁺ and HCO₃⁻ constitute the second group which affects the salinity of groundwater in the region. This is studied with the relationship Ca²⁺ vs HCO₃⁻ and Ca²⁺+Mg²⁺ vs SO₄²⁻+HCO₃⁻ diagrams as show in Fig. 6. For the first case, the most common weathering reaction in the case of carbonates is simple dissolution, giving a 1:2 ratio of Ca:HCO₃⁵⁶. According to Kumar⁵⁷ low molar ratios (<0.5) of Ca/HCO₃ indicate exchange of calcium and magnesium in water by sodium bound in clay and/or cation exchange or HCO₃ enrichment possibly from silicate weathering. On the contrary, high ratios (>0.5) suggest other sources for Ca²⁺ and Mg²⁺, such as reverse ion exchange, which was observed in hard rock formations with an increase in salinity. For the second case, when the ionic concentrations falls above the equiline, then it is as a result of carbonate weathering and when the ionic concentrations falls along the equiline then it is as a result of both carbonate weathering and silicate weathering and when it fall below the equiline then it is as a result of silicate weathering⁵⁸. It is therefore clear that the chemistry of the water in the region is generally influenced by the carbonate weathering of Cretaceous and silicate weathering formations of Quaternary age. For carbonate weathering the process occurs according to the Eq. 6-8⁵⁴:

$$CO_2 + H_2O \leftrightarrow H_2CO_3$$
 (6)

$$H_2CO_3 \leftrightarrow HCO_3^- + H_3O^+$$
 (7)

$$CaCO_3 + H_2O + CO_2 \leftrightarrow Ca^{2+} + 2HCO_3^{-}$$
(8)

For silicates weathering, the attack of the silicate mineral by H_2CO_3 from dissolution of atmospheric CO_2 and soil or H_2SO_4 from the oxidation of sulphides, frees Na⁺, Ca²⁺ and K⁺ as Eq. 9-12⁵⁹. The pH increase promotes these Eq. 9-12⁶⁰:

$$NaAlSi_{3}O_{8}+H^{+}+7H_{2}O\rightarrow 3H_{4}SiO_{4}+Al(OH)_{3}+Na^{+}$$
(9)

$$CaAl_2Si_2O_8 + 2H^+ + 6H_2O \rightarrow 2H_4SiO_4 + 2Al(OH)_3 + Ca^{2+}$$
(10)

$$KAlSi_{3}O_{8}+H^{+}+7H_{2}O\rightarrow 3H_{4}SiO_{4}+Al(OH)_{3}+K^{+}$$
(11)

$$4Al(OH)_{3}+2NaAlSi_{3}O_{8+}H_{2}O \rightarrow 3Al_{2}Si_{2}O_{5}(OH)_{4}+2Na^{+}+OH^{-}$$
(12)

Calcium and magnesium are dissolved from practically all solids and rocks, but especially from limestone, dolomite and gypsum and are found in large quantities in some brine⁶¹. The calcium ion concentration present in the groundwater of the study area might have come from the dissolution of CaCO₃ and CaMg (CO₃)₂ during recharge. Hard water is unsuitable for domestic use, as well as hardness of water limits its use for industrial purposes; causing scaling of pots, boilers and irrigation pipes may cause health problems to human, such as kidney failure⁵⁵.

Water with SSP greater than 60% may result in sodium accumulations that will cause a decrease of the soil's physical properties⁵⁵. When the concentration of sodium is high in irrigation water, sodium ions tend to be absorbed by clay particles, displacing Mg²⁺ and Ca²⁺ ions. This exchange process of Na⁺ in water for Ca²⁺ and Mg²⁺ in soil reduces the permeability and eventually results in soil with poor internal drainage. Hence, air and water circulation is restricted during wet conditions and such soils are usually hard when dry⁵⁷. The calculated values of SSP varied from 15-70% indicating well to unsuitable degree of restriction on the use of this wastewater



Fig. 7(a-b): (a) Wilcox diagram and (b) Permeability index

in irrigation (Fig. 7a). The water of good to doubtful quality is situated on the boundaries of the plain while the water for doubtful to unsuitable quality is at the center of the plain. The boundaries area is with low salinity while the area center is with high salinity.

For the Permeability Indices (PI), the maximum value of PI is 72.2%. Hence, all the samples fall under class I and reflect suitability for irrigation purposes (Fig. 7b).

CONCLUSION

The study of the quality of groundwater from the Djacer spring shows that water with high salinity concerns the center of the plain while low salinity water is located in the vicinity of the carbonate formation in the plain boundary. This characteristic seems to be related to the low groundwater flow allowing an increase in matrix leaching and dissolution by water–rock interaction processes within the aquifer.

SIGNIFICANCE STATEMENT

This study has shown the distribution of water quality for drinking and irrigation using major ions chemistry in the arid region of Djacer spring. It has also helped to precise the areas of good water quality for a better management since it is getting increasingly scarce.

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