



RESEARCH PAPER

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Groundwater quality and its suitability for drinking and agricultural use in Tebessa watershed (Northeastern of Algeria)

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Abstract

The study of the water quality in the alluvial aquifer of Tebessa basin is necessary to perform an assessment of the hydrogeochemical quality, their uses and the origin of their pollutant. Thus, a thorough understanding of aquifer behaviour and water mineralization origin using geochemical tools can lead to relevant information regarding mineralisation processes, groundwater chemistry, and their uses. The results show that groundwater is saline with a dominant chemical facies "Magnesium Sulfate". The relationships established between the concentrations in major elements allowed a better characterization of the waters of the studied aquifer, in particular the mode of acquisition of the mineralization. The latter is mainly caused by the evaporitic minerals (gypsum, anhydrite and halite) which are under-saturated and can dissolve further, thus causing the increase of the overall concentration. While carbonate minerals are supersaturated and tend to precipitate. The evolution of nitrate levels shows a deterioration of the natural state of the groundwater by a pollution linked to the agricultural activity by the excessive use of the fertilizers. Despite this chemical diversity, water is generally suitable for human consumption, with the exception of wells located near farms. Also over than 50% of samples are suitable for irrigation use.

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Introduction

The assessment of groundwater quality is as important as its quantity for various purposes ranging from domestic, industrial and agricultural uses all over the globe (Subramani and Damodarasamy 2005). The quality of groundwater in a particular region is a function of physical, chemical and biological parameters that are greatly influenced by geological formations and anthropogenic activities.

Hydrochemistry has made significant contributions to the understanding of groundwater evolution (Li *et al.* 2008; Dar *et al.* 2014). Groundwater carries chemical signatures of recharge water and interaction with minerals and sediments forming aquifers along the flow paths as well as anthropogenic activities (Yangui *et al.* 2011; Monjerezi *et al.* 2012; Voutsis *et al.* 2015).

The plain of Tebessa lies in the semi-arid region of Algeria, where the precipitation ranges from 300 to 600mm. Summer temperatures can reach 40°C. This situation of dryness accentuates the drawdown of water resource especially during the last decade. In addition, the region of Tebessa and the surrounding villages (Bekkaria, Hammamet) have seen a great deal of growth with the establishment of new industries and farms. All of these factors generate sometimes very unfavorable effects on waters quality generally causing increased salt content (Rouabhia *et al.* 2009).

Given this context, the present paper aims to evaluate the groundwater chemistry and groundwater quality in the plain of Tebessa and its suitability for drinking and irrigation purposes and to understand the causes and mechanisms controlling the groundwater chemistry.

Material and methods

Studied area

The study area is located in the eastern Algeria in the wilaya of Tebessa, about 230km south of the Mediterranean coast. This watershed is limited to the south by El Oued, to the west by Constantine, to the north by Souk Ahras and to the east by Algero-Tunisian boundary (Fig. 1).

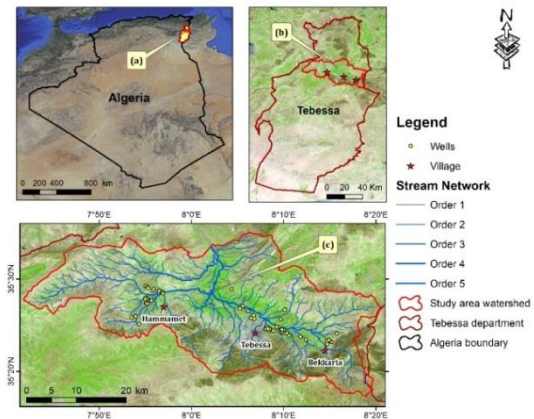


Fig. 1. Tebessa watershed and its location: (a) location in Algeria; (b) location in Tebessa province; (c) Study area watershed.

The study area is considered semi-arid climate, the annual precipitation vary from 307 to 625mm for the period 1972-2009 (Ghrieb, 2010), characterized by irregular yearly distribution. The mean monthly temperatures are high, varying between 6°C in January and 40°C in July with a mean annual value about 29°C. The mean annual potential evapotranspiration, according to the C. W. Thornthwaite formula is approximately 750mm (Drias, 2013).

As for the surface flow (El Kebir, Chabro and Ksob), the network allows natural drainage of the plain. The geology of the region (Bles and Fleury, 1970; Vila, 1980) is constituted in the major part by cretaceous formations, forming a series of anticlines and synclines. The stratigraphic sequence is presented in the form of alternation of carbonated formations of limestones, marly limestones, and argillaceous marls (Fig. 2).

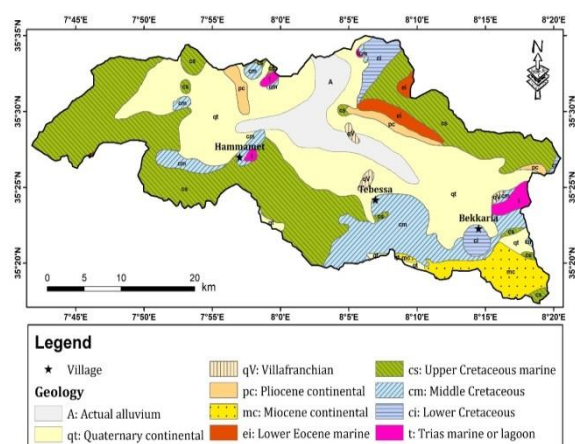


Fig. 2. Geological map of the study area.

The central part (tectonic depression of Tebessa) is covered by the plio-quaternary. This depression separates the highlands of Dyr situated in the North from the one of Doukkane and Mestrie highlands in the South.

The Tebessa area straddles two groundwater level aquifers; the limestone aquifer, and the alluvial aquifer. In general, the shallow groundwater area is found in the alluvial fan deposits from plioquaternary age. This aquifer is overlying geologic formations consist of cenomanien marly layers and form aquicludes. The recharge to the aquifer takes place in the highlands of Dyr, Bouroumane from east and Doukkane from the west.

This aquifer of great extension occupies the major part of the tectonic depression, limited at the West and at the East by two great faults of NW-SE orientation. It is consisted very varied deposits such as, alluvial fans, silts, calcareous crust, conglomerates, and gravels. This aquifer plays an important role in the supply of drinking water for the inhabitants of this area (Fehdi *et al.*, 2009).

In general, the water table surface has the same morphology as topography (Sedrati and Djabri, 2014). Two major directions of flow: the first east to west direction is from Bekkaria to Tébesa; the second direction is north to south. To the east, the piezometric lines are generally regular, indicating a hydraulic gradient of the order of 0.05. In the central area, the curves indicate a low hydraulic gradient of the order of 0.002. It is thought that the variation of the hydraulic gradient is mainly due to the heterogeneity of the lithology. It was noted that a much accentuated depressive zone was located at the north of Ain Chabro. This is generated by the exploitation of drillings and wells in this part, with more than 30 wells in the exploitation listed in the study area. In a large part the waters converge towards Kabir watercourse, which plays the role of a drainage axis at the superficial aquifer. A total of 50 groundwater samples were collected from the study area during September 2015 from three different locations of Tebessa watershed. The sampling

locations are mentioned in the Fig. 3: Bekkaria (13 wells), Tebessa (20 wells), Hammamet (17 wells) and preserved as per the methods prescribed (Rodier *et al.*, 2009). We have chosen physicochemical parameters such that the electrical conductivity ($\mu\text{S}/\text{cm}$) and the pH that are measured on site directly after sampling with a multiparameter WTW, while rests of the parameters were analysed in the laboratory such as the major elements soluble. These elements are analysed in the laboratory by titrimetry for Chlorides (Cl^-), Bicarbonates (HCO_3^-) and Calcium (Ca^{2+}), by complexometry for total hardness (TH), by spectrophotometry for sulphates (SO_4^{2-}), by flame photometry for Sodium (Na^+) and Potassium (K^+) and by colorimetry for Nitrates (NO_3^-).

The magnesium (Mg^{2+}) concentration of the water analyzed is given by the difference between the total hardness and the calcium hardness $\text{mg}^{2+} = \text{TH} - \text{Ca}^{2+}$ (Rodier *et al.*, 2009). All the chemical concentrations are expressed in mg/l (Table 1).

Table 1. Physico-chemical characteristics of the analyzed elements.

Parameters	Statistical Parameters				WHO standards
	Mean	SD	Minimum	Maximum	
pH	7.93	0.27	7.00	8.66	≥ 6.5 $\text{et} \leq 9$
CE ($\mu\text{S}/\text{cm}$)	2444.54	1310.10	900	6800	1000
TDS (mg/l)	1518.20	819.85	558.00	4216.00	< 600
Ca^{2+} (mg/l)	126.25	101.11	43.00	520.00	200
Mg^{2+} (mg/l)	117.25	57.96	29.00	305.00	150
Na^+ (mg/l)	195.29	173.02	62.00	840.00	200
K^+ (mg/l)	5.82	6.63	1.00	40.00	12
HCO_3^- (mg/l)	310.00	82.18	171.00	580.00	/
Cl^- (mg/l)	275.00	258.82	60.35	1199.90	250
SO_4^{2-} (mg/l)	546.18	454.89	140.00	2800.00	500
NO_3^- (mg/l)	56.78	44.87	6.00	160.00	50

Concentration of major ions are also generally high (Table 1). To verify the analytical error of analysed ion concentration, electroneutrality (ionic balance) was computed by following equation:

$$E = (\Sigma \text{cation} - \Sigma \text{anion}) / (\Sigma \text{cation} + \Sigma \text{anion}) * 100 \quad (1).$$

where the sum of major cations and anions are expressed in meq/L and E is the error percent/reaction error/ cationic and anionic balance. The value taken is limited to $\pm 10\%$ (Hem, 1975).

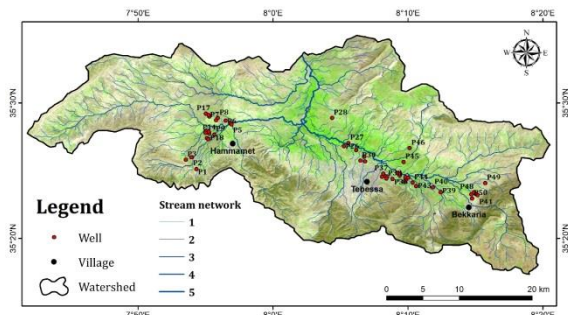


Fig. 3. Location of analysis samples.

Mechanism controlling groundwater chemistry

Hydrogeochemical studies relevant to the water quality explain the relationship of water chemistry to aquifer lithology. Such relationship would help not only to explain the origin and distribution of dissolved constituents but also to elucidate the factors controlling groundwater chemistry (Rengarajan & Balasubramanian, 1990).

Hydrochemical facies

To know the hydro-geochemical regime of the study area, the analytical values obtained from the groundwater samples are plotted on Piper tri-linear diagram (Piper, 1994). This diagram is used to infer hydro geochemical facies. Hydrochemical facies are distinct zones that possess cation and anion concentration categories. The Piper tri-linear graphical representation of chemical data of representative samples from the study area reveal the analogies, dissimilarities and different types of waters in the study area. This clearly explains the variations or domination of cation and anion concentrations during the season.

Basic exchange index (b.e.i)

The basic exchange index (b.e.i) defined by Schoeller (1956); translates the ratio between the ions exchanged and the originally existing ions of the same nature in the water. It makes it possible to highlight the evolution of the chemical process of water during its underground course.

The index is calculated by the following formula:

$$b.e.i = (rCl - r(Na^{+} + K^{+})) / rCl \quad (2)$$

According to the values of this index, we have:

Exchange of Ca^{2+} and Mg^{2+} ions of water by the Na^{+} and K^{+} ions of the host formations; if the b.e.i is of negative sign.

Replacing the Na^{+} and K^{+} ions of the water with Mg^{2+} and Ca^{2+} ions of the host formations; if the index b.e.i is of positive sign.

A balance between the chemical components of the water and those of the surrounding land for a zero b.e. index.

Saturation index (SI)

Saturation indices were calculated using the computer program PHREEQC (Parkhurst and Appelo, 2013). The saturation index (SI) indicates the degree of disequilibrium of a solution with respect to a certain mineral; if a solution is at equilibrium with a given mineral, the mineral will not dissolve or precipitate. The saturation index with respect to a certain mineral (such as calcite) can be used to determine the likelihood of a mineral or phase dissolving into or precipitating from a solution. A negative (-) saturation index indicates that the solution is undersaturated with respect to the mineral. If the solution is undersaturated, it has the potential to dissolve the mineral if it is present and kinetics allow. If a saturation index is positive (+), the solution is oversaturated with respect to a mineral and there is the potential for the mineral to precipitate, a saturation index near zero indicates that the solution is near equilibrium with the mineral reacting fast enough to maintain equilibrium.

Saturation indices are calculated with respect to certain minerals. The saturation index (SI) is the log of the ion-activity product of a solution divided by the solubility product (Ksp) (Drever, 1997). For example, the saturation index of calcite ($CaCO_3$) is:

$$SI = \log(Ca^{2+}(CO_3^{2-})/Ksp(calcite)) \quad (3)$$

Where $[Ca^{2+}]$ is the activity of the calcium ion, $[CO_3^{2-}]$ is the activity of the carbonate ion, and Ksp is the solubility product of calcite.

Concentration diagram

This type of diagram makes it possible to follow the evolution of the concentration of the dissolved elements with respect to a reference element chosen as a tracer. It aims to highlight the chemical mechanisms (dissolution precipitation, ion exchange ...) likely to control the evolution of the concentration of the various elements.

The concentration diagrams of solute X is a graph of $\log[X]$ as a function of $\log$ concentration factor (CF). CF under natural conditions can be estimated by using a reference tracer whose properties have been checked in the context of the study (Gac, 1980; Barbeiro *et al.*, 2004; Ribolzi *et al.*, 1996). Its values are then estimated as the ratio between the tracer content in sample i and the tracer content of the most diluted solution involved d. Taking into account preliminary data, concentration diagrams were constructed by using X as a tracer,

$$CF_i = X_i/X_d \quad (4)$$

With X_i the tracer content in sample i.

X_d the tracer content of the most diluted solution.

The concentration factor (FC) of the waters of this layer is estimated from the chloride (Cl) used here as a tracer. This element has been preferred over other elements for two reasons:

In the concentration range, studied chlorine can be considered inert with respect to the porous matrix and therefore it does not enter into chemical processes that can affect its concentration. It can therefore be a criterion for estimating the concentration factor.

In addition, this element has the steepest slope in the concentration diagram; which shows that it is the parameter least affected by biogeochemical processes.

Water Quality Assessment

Quality for Drinking Water Supply

In the present study, water quality for Drinking Water Supply (DWS) were determined and the results were compared with the values prescribed in water quality standards in World Health Organization (WHO, 2017).

Suitability of water for irrigation

Water with high salinity is toxic to plants and poses a salinity hazard. Soils with high levels of total salinity are called saline soils (McFarlane and Williamson, 2002). High concentrations of salt in the soil can result in a "physiological" drought condition. That is, even though the field appears to have plenty of moisture, the plants wilt because the roots are unable to absorb the water. Water salinity is usually measured by the TDS (total dissolved solids) or the EC (electric conductivity).

Irrigation water containing large amounts of sodium is of special concern due to sodium's effects on the soil and poses a sodium hazard. Sodium hazard is usually expressed in terms of SAR or the sodium adsorption ratio. SAR is calculated from the ratio of sodium to calcium and magnesium (Alrajhi *et al.* 2015). The latter two ions are important since they tend to counter the effects of sodium.

The sodium adsorption ratio (SAR) was calculated by the following equation given by Richards (1954):

$$SAR = Na / ((Ca + Mg) / 2)^{0.5} \quad (5)$$

Where, all ion concentrations are expressed in meq/L.

SAR was plotted against EC ($\mu S/cm$) on the US salinity diagram to categorize the analyzed water samples according to their irrigational suitability quotient. Five classes of water have been defined: excellent, good, acceptable, poor, bad (Table 2).

Result and discussion

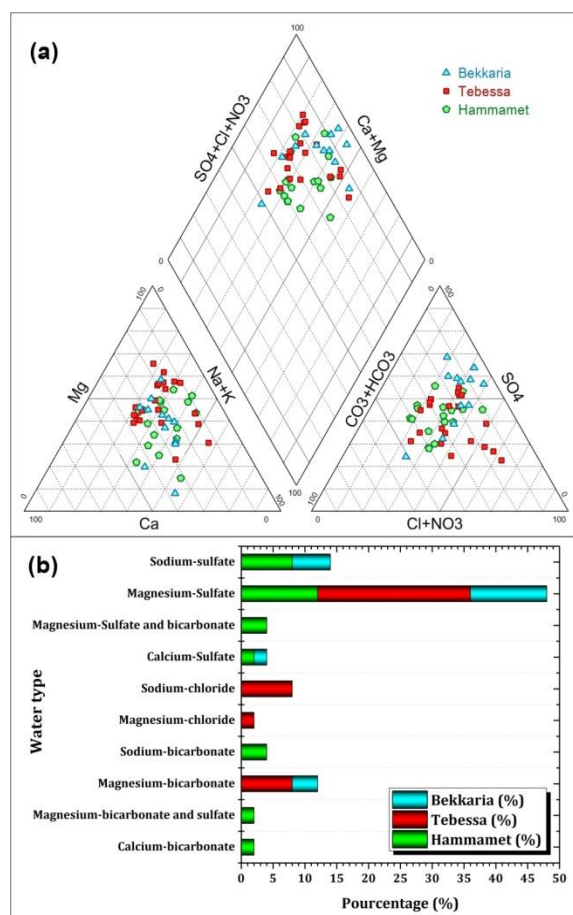
Mechanism controlling groundwater chemistry

Hydrochemical facies

The ionic relation between hydrochemical parameters was studied by plotting major cations and anions in the Piper's tri-linear diagram (Fig. 4). The results show a variability of the chemical facies of waters. Samples in Tebessa and Bekkaria cities are characterized by the dominance of sulfate, chloride, magnesium and sodium. As a result, magnesium sulfate is the dominant facies. We can find in second place sodium sulfate facies in Bekkaria, and sodium chloride in Tebessa city. In Hammamet city, water is dominated by the same ions but have relatively higher concentrations of bicarbonate.

Table 2. Classification of Water by Degree of Irrigation Ability Using the SAR Method (The Worker, 1976).

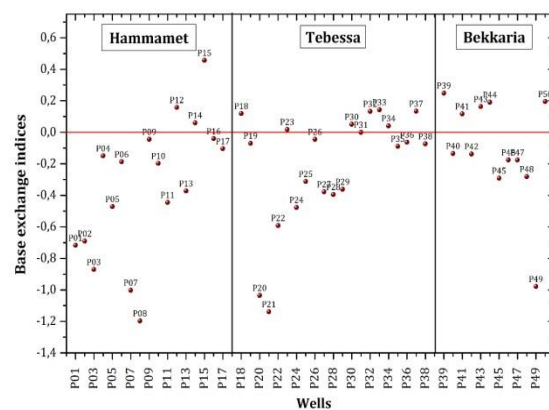
Degree	Quality	Class	State of use
1	Excellent	C1-S1 C1-S2	Safe use for irrigation of most crops on most soils.
2	Good	C2-S1 C2-S2	Suitable for plants that have tolerance to salts, however its use can cause problems for clays.
3	Acceptable	C3-S1 C2-S3 C3-S2	Salinity must be controlled, irrigation of tolerable crops to salts on well-drained soils.
4	Poor	C4-S1 C4-S2 C3-S3 C3-S4	Highly mineralized water, used only for very salt-resistant plants with good soil permeability.
5	Bad	C4-S3 C4-S4	Unusable

**Fig. 4.** Water types: (a) Piper's diagram. (b) chemical facies.

Basic exchange index (b.e.i)

The values of b.e.i. (Fig. 5) show that most part of water samples in Hammamet city has a negative value; this means that water receives Na^+ and K^+ released from

alluvial deposits that contribute to groundwater chemistry. The sodium sulfate presents as second chemical facies dominant in the water of this city. The same result was found in Tebessa and Bekkaria cities but with higher numbers of water samples, which have the inverse state (positive value). For this reason, the water contain a mixture of Na^+ , K^+ , Mg^{2+} and Ca^{2+} ions that given water a different chemical facies.

**Fig. 5.** Basic exchange index.

Saturation index (SI)

Groundwater saturation state was computed using PHREEQC program. The results showed that most of groundwater samples were in an undersaturation state ($\text{SI} < 0$) with respect to halite, gypsum and anhydrite minerals, but in an oversaturation state ($\text{SI} > 0$) with respect to calcite, aragonite and dolomite (Fig. 6), indicating that groundwater chemical

composition was contributed by halite, gypsum and anhydrite dissolution, not calcite, aragonite and dolomite dissolution. Anhydrite and Gypsum are close to equilibrium and tend towards saturation.

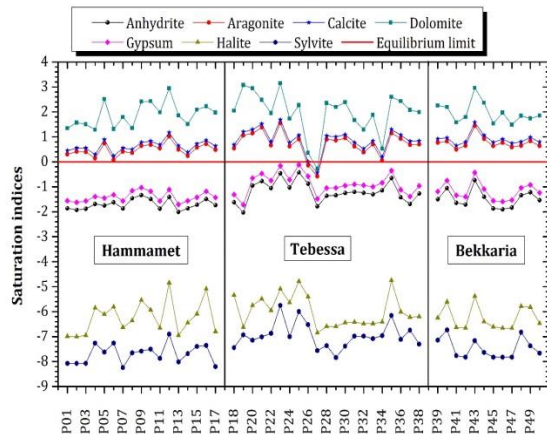


Fig. 6. Variation of the saturation index.

Concentration diagram

The concentration diagram (Fig. 7) shows that the sodium concentration does not increase at the same rate as chloride (Fig. 7). This highlights the phenomenon of ion exchange, which slightly affected the concentration of this element. Indeed, the fixation of sodium by clays is at the origin of the decrease in the Na/Cl ratio

- Calcium molality increases less strongly than sulphate because part of Ca^{2+} is involved in the precipitation of calcite. Calcium thus becomes the limiting factor in the conjunctive precipitation of calcite and gypsum (Droubi 1976; Valles *et al.* 1989).
- Alkalinity and Calcium content do not simultaneously increase; this is due to the precipitation of calcite (Valles *et al.* 1989). Indeed, the analysis of the saturation index with respect to calcite shows that the majority of the water sampled is saturated or even supersaturated with respect to the mineral, with the exception of a few samples that are slightly under-saturated (Fig. 6).
- Magnesium generally varies in the same direction as Calcium.
- Potassium and Nitrates show practically the same behaviour of molalities in relation to the total concentration.

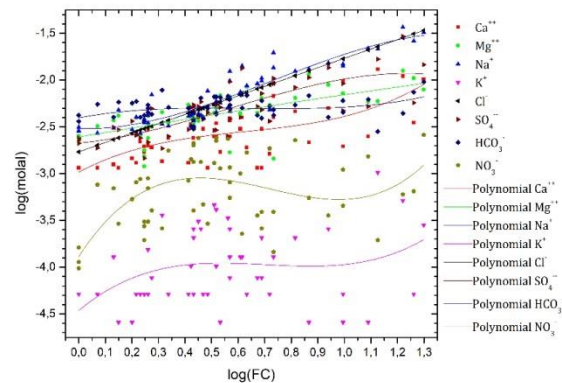


Fig. 7. Concentration diagram.

Water Quality Assessment

The purpose of this section is to characterize groundwater for both domestic as well as for irrigation purposes.

Groundwater quality for drinking purposes

The cations variation diagram (Fig. 8) shows that the average calcium concentration exceeds the WHO drinking standard, however, most water samples have concentrations below the standard.

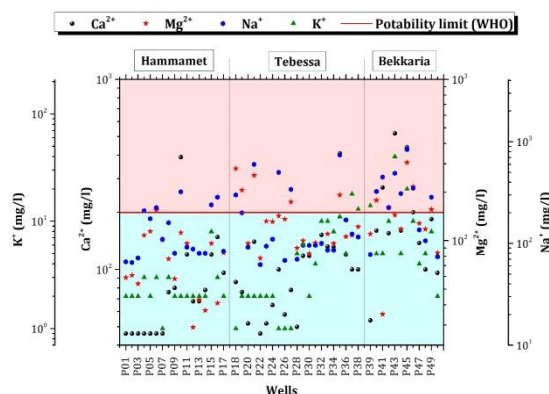


Fig. 8. Cations variation diagram.

Thus only a few wells indicate high concentrations exceeding the norm, as is the case of P10 in Hammamet; in the Merdja plain and the wells P34, P45 and P47 in Bekkaria city. Most of these concentrations are related to the dissolution of the gypsum of Djebel Djebissa and the basic exchange with alluvial deposits. The averagemg concentration is around 117.25mg/l; most of the values are in conformity with the drinking water standards (WHO), except for the wells (19, 20, 28, 36) in the

north-east of the city of Tebessa and the wells (42, 47, 48, 51) in the northwest of Bekkaria. The high concentrations of magnesium are due to the dissolution of dolomitic limestones on the edges.

The highest sodium values are found in the eastern zone (Bekkaria region) and in the centre of the Tebessa plain, which is the result of the basic exchange phenomenon.

Most samples clearly show that the K value is low and does not exceed the potability standard except for the wells (38 and 39) in Tébéssa and the wells (41, 45, 47) in Bekkaria city.

The anions variation diagram (Fig. 9) Chloride values are variable, with some high concentrations (exceeding the recommended standard of 250mg/l). These high grades are located in the centre of the plain (P19, P22, P25, P26, P36); the wells (43, 45, 46, 47, 48, 51) in Bekkaria.

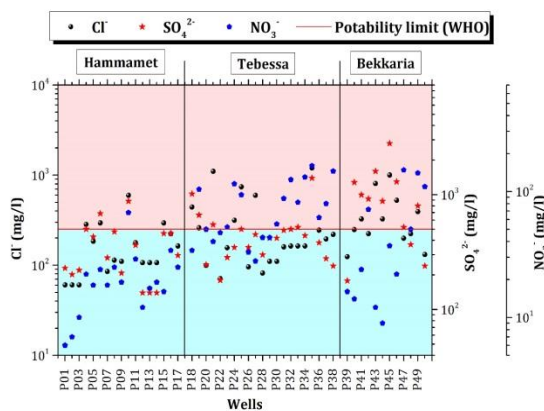


Fig. 9. Anions variation diagram.

These high values are due to the leaching of sediments from the marl and dolomitic limestones on the edge on the one hand and the leaching of quaternary sediments covering the area on the other hand. The presence of alluvium and sediments of evaporative origin on surface facilitates soil leaching. In the Hammamet area, except for the wells (4, 6, 15), the other wells have concentrations that conform to the standard. Quaternary clays are at the origin of these concentrations; the disposition of these formations on the surface of the soil favours their leaching. In

Tébessa, the waters contained in alluvial formations which are rich in soluble salts are at the origin of this increase, we can also explain these increases in chlorides by pollution from domestic and agricultural sources. In the Bekkaria and Tebessa area, high sulphate values exceed the recommended standard in some wells, leaching of gypsum formations from Djebel Djebissa is at the origin of these concentrations, on the one hand, and anthropogenic inputs from sulphated chemical fertilizers, on the other hand. These concentrations decrease when going to Hammamet city and can exceed the norm at the wells (6 and 10), the quaternary clays are at the origin of these values. These high values are due to the leaching of marl and dolomitic limestone from the edge and to the leaching of quaternary sediments covering this area. The presence of alluvial deposits and sediments of evaporite origin on the soil surface facilitates leaching. In Bekkaria, the arrangement of quartz sand and pliocene age clays on the surface favours their leaching.

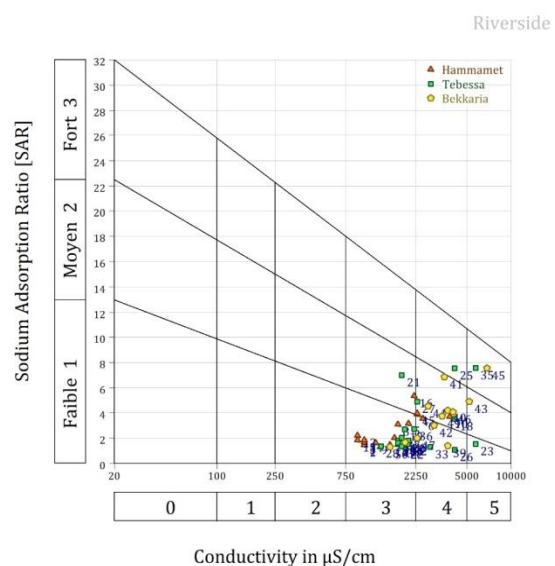


Fig. 10. Plots of groundwater samples in RIVERSIDE diagram.

It is also noted that 36% of the samples analysed have high concentrations of Nitrates exceeding the drinking standards with a maximum value of around 160mg/l. This indicates pollution of this water, which is related to several factors, the most important of which is agricultural activity, where excessive use of

fertilizers contributes to the increase in nitrate levels (Rouabhia *et al.* 2009). Other factors can influence in one way or another, such as pastoral activity, poor well protection and lack of sanitation networks. The waters most exposed to pollution by Nitrates are the surface waters of the areas surrounding the city of Tébessa and Bekkaria.

Groundwater quality for irrigation purpose

Assessment of groundwater quality for irrigation has been analyzed using the classic diagram RIVERSIDE (Fig. 10) which is combined between the values of electrical conductivity and SAR to highlight the classes that present a danger of alkalinity.

The water of the region generally is classified into three categories C3, C4 and C5 with a medium to very high risk of salinization. For The sodium hazard, the water is found confined in three groups S1, S2 and S3 with low to high alkalinity hazard. Consequently, eight classes can be determined: C5S1, C4S1 and C3S1, C5S2 and C4S2, C3S2, C5S3 and C4S3. As a result, 54% of the samples coming within the subfield of 'Good to Permissible' category, and 37% of wells present a danger of both sodicity and salinity. In addition, some wells (9%) were unusable for irrigation.

Conclusion

The hydrochemistry data in Tébessa region have provided helpful insights into groundwater quality of the shallow aquifer that can be used to find out the groundwater suitability for domestic and agricultural purposes. The groundwater quality reveals that the conductivity values present danger for drinking while the water has high salinity due mainly to the concentration of sulphates and magnesium that gives to water SO₄-Mg type. Over than 50% of water samples are not affected by the salinity and sodium hazard, so they are suitable for irrigation purpose.

The relationships established between the concentrations of major elements allowed for a better characterization of the water, in particular the mode of acquisition of mineralization. This latter is mainly controlled by the geochemical processes of dissolution and/or precipitation (dissolution of

calcite upon entry of the water into the aquifer, then dissolution of dolomite accompanied by precipitation of calcite within the aquifer) and by basic exchanges with clay minerals.

The evolution of the molality logs of the major elements as a function of the log of the concentration factor (CF) shows that the salinity of these waters is caused by evaporate minerals (gypsum, anhydrite and halite), and especially by largely under-saturated halite which can dissolve further, thus causing the overall concentration to increase. While the elements derived from carbonate minerals do not evolve in proportion to the log concentration factor and participate in precipitation.

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