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Geochemistry of the interaction nitrate-soluble salt water a salty environment for Lake Fetzara (Algerian Northeast)

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Abstract

The lake Fetzara is 18 km from Annaba, it was officially classified as a wetland protected by the Ramsar Convention (2003). The waters of the lake and soils are affected by salinization. The objective of this work is to locate the salinity levels of surface and ground waters of Lake Fetzara and bring out relationships soluble salts - nitrates that may exist. To interpret the results of physicochemical water, diagrams of Piper and Richards are used to determine the chemical composition and water facies and their suitability for irrigation. The study will be punctuated by a PCA statistical analysis that will monitor relationships between different variables. The results show that salinity is higher with values between 100 and 7500 µS/cm , on the level of the South-eastern zone of the lake with a chlorinate-sodic and potassic, with sulfated sodic chemical facies The statistical approach from PCA shows that the processes responsible for salinization of the lake is the concentration of the latter under the effect of evaporation and confirms the positive relationship between nitrate and soluble salts in water surface and negative in groundwater. The high concentration of nitrates in surface waters is mainly due to the use of fertilizers on the agricultural area and the contribution by rainwater and runoff.

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Introduction

The Earth's atmosphere is composed of about 78.1% nitrogen gas (Mariotti, 1982). All forms of nitrogen (organic nitrogen, ammonium, nitrites,..etc.) can be the source of nitrate by a biological process *(*Pauwells *et al,* 1996). The amounts of nitrogen taken annually by plants vary widely up to over 100g m2/year (Bowden, 1987). The vegetation type is the cause of this variability (Ruffinoni, 1994), which depends on the plant biomass and the water column of the nutrient concentration and the substrate. Nitrogen applications are more serious in the spring during plant growth (Mitsch et Gosselink, 1993). Releases communities and occasionally some industries (fertilizers, explosives and oxidants) may also contribute to the enrichment of nitrates in surface waters. Often nitrates seeping into the soil through leaching and eventually pollute groundwater and rivers also (Debieche, 2002). The increase is particularly significant concentrations in some layers and varies inversely with depth.

In Lake Fetzara, the phenomenon of salinity increases from one year to another due to several particularly climatic and anthropogenic factors. This study was conducted to check the current status of the chemistry of surface and ground waters of Lake Fetzara and evaluate the interaction of nitrate ions (NO_3^-) with the major soluble salts waters of this site and their origin.

Materials and methods

The period of withdrawals took place in December 2013, for a total of 31 samples, referring to surface waters (18 samples) and ground (13 samples) of Lake Fetzara.

The analysis of chemical elements was performed according to standard analytical methods (Rodier *et al,* 2009):

- Chloride (Cl^-), *by titration (Mohr method)*;
- carbonates (CO_3^{--}) and Bicarbonate (HCO_3^-) *by titration with sulfuric acid*
-Sulfates (SO_4^{--}), gravimetry by *$BaCl_2$*
- Nitrite (NO_2^-) *spectrophotometry*. by *réactif of Zambelli (Rodier, 2009)*
- Nitrate (NO_3^-) *spectrophotometry*. by *salicylate of sodium (Rodier, 2009)*
- ammonium (NH_4^+) by *spectrophotometry;* by *réactif of Nessler (Rodier, 2009)*
- Calcium (Ca^{++}) and Magnesium (Mg^{++}) *by complexometric EDTA*;
- Sodium (Na^+) and Potassium (K^+) by spectrophotometry at flame.

To interpret the results of physicochemical water, diagrams of Piper and Richards are used to determine the chemical composition and water facies and their suitability for irrigation. The study will be punctuated by a PCA statistical analysis that will monitor relationships between different variables.

The salinity of the waters and soil of the lake has been the subject of a (Djamai, 2007 and 2011, zahi, 2014, fekrache, 2015) which are compared with our results.

Characteristics of the study area

The Lake Fetzara is located in the North East of Algeria; it is located 18 km southwest of the city of Annaba. It stretches 17 km from east to west and 13 km from north to south with an area of about 20,680 ha (Fig. 1).

Geologically, the lake is part of the entire North Eastern Tell Algeria, which extends from the region of Constantine on the Algerian-Tunisian border. The lake Fetzara is a vast depression bordered to the north by the massive Edough, consisting of a variety of age Precambrian metamorphic rocks and Paleozoic (Laouar *et al.*, 2002). Petrological and geochemical studies indicate that these are ancient igneous rocks in calc-alkaline character (Zahi, 2013). The lake is bordered to the north by the head of the commune Berrahal, south by the municipalities of the territory of El Eulma and Cheurfa and east the small villages of Wadi Zied and El Gantra (Fekrache, 2015).

Hydrologically, rivers in the Lake Fetzara region are characterized by a very irregular regime, torrential in winter and dry in summer. Networks in surface water are formed by a branching of the free extended; the beds of these rivers are widened in parts swallow, that is to say in contact with the lake.

Wadi El Hout South, Wadi Melah in the West and the Wadi Zied the Northeast are the three main wadis feeding Lake Fetzara, and Wadi Meboudja that ensures water drainage. This area is subject to a Mediterranean climate characterized by two distinct seasons, a cool and wet and the other hot and dry.

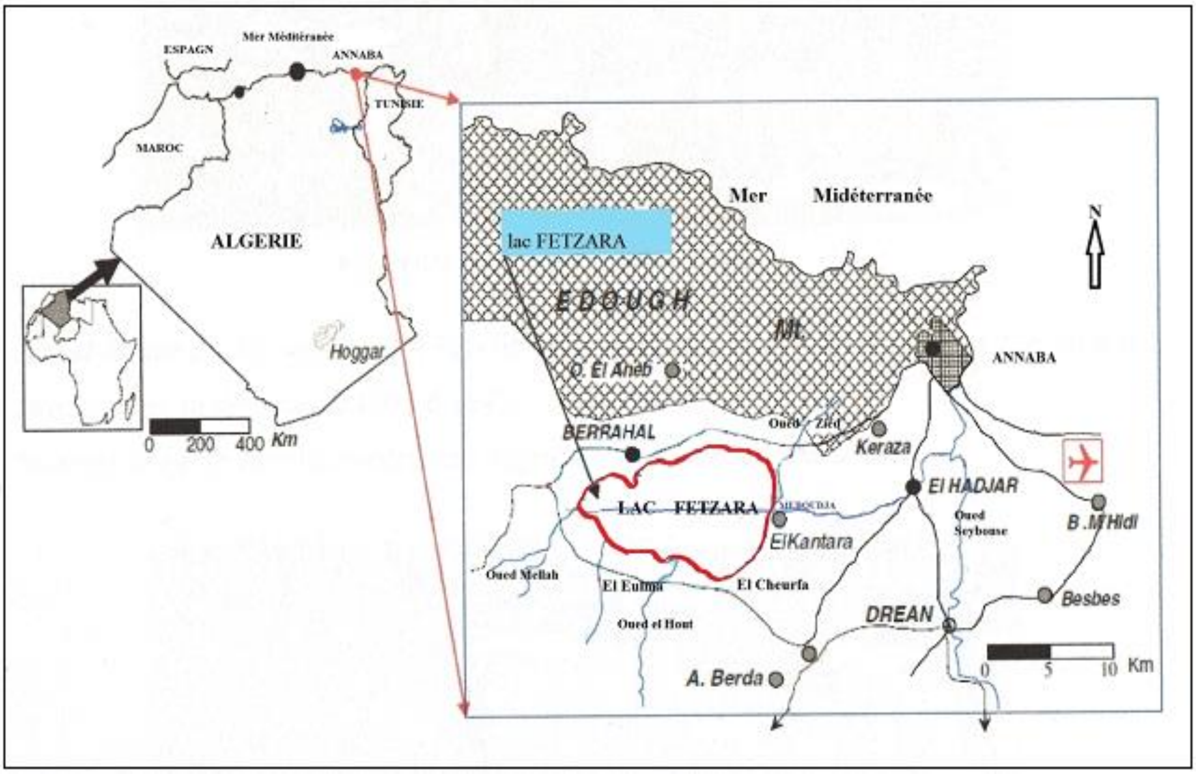

Fig. 1. Geographical location lake Fetzara.

Results and discussion

Geochemical study of water

Electrical conductivity: The results of surface waters show significant variability in the electrical conductivity with values between 100 and 7500 µS/cm; however the majority of samples are in the range 100 to 2000 µS/cm (Fig. 2).

Table 1. Correlation coefficient (R2) between the nitrates and other soluble salts.

	Correlation coefficients R2	
Variables	Surface water	Groundwater
CE	0.65	-0.10
Cl^-	0.70	-0.22
Na^+	0.30	-0.31
K^+	-0.20	0.31
Ca^{++}	0.50	0.35
Mg^{++}	0.46	-0.12
CO_3^{2-}	-0.18	-0.26
HCO_3^-	-0.32	-0.26
SO_4^{2-}	0.32	-0.13
pH	-0.053	-0.46
NO_2^-	0.64	0.41
NH_4^+	-0.09	-0.08

Groundwater has electrical conductivity values ranging from 200 to 3000 µS/cm (Fig. 3). The salinity of surface water is greater than that of groundwater. Several studies show that the salinity of the lake water and especially that surface water is mainly due to the concentration of these water through evaporation phenomenon linked to the climate of the region is hot and dry, especially during the summer season (Zahi, 2014).

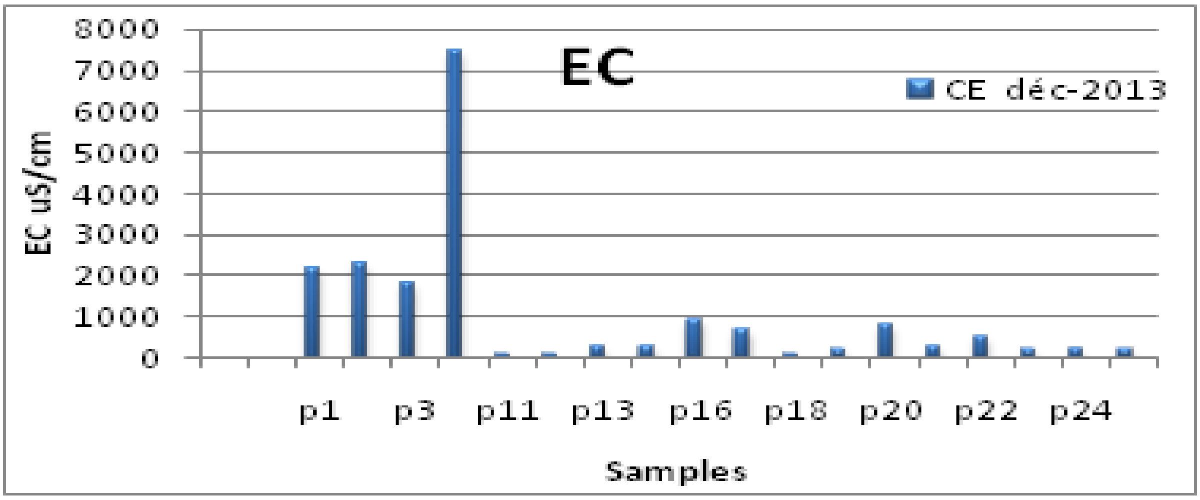

Fig. 2. Changes in the electrical conductivity (EC) of surface waters.

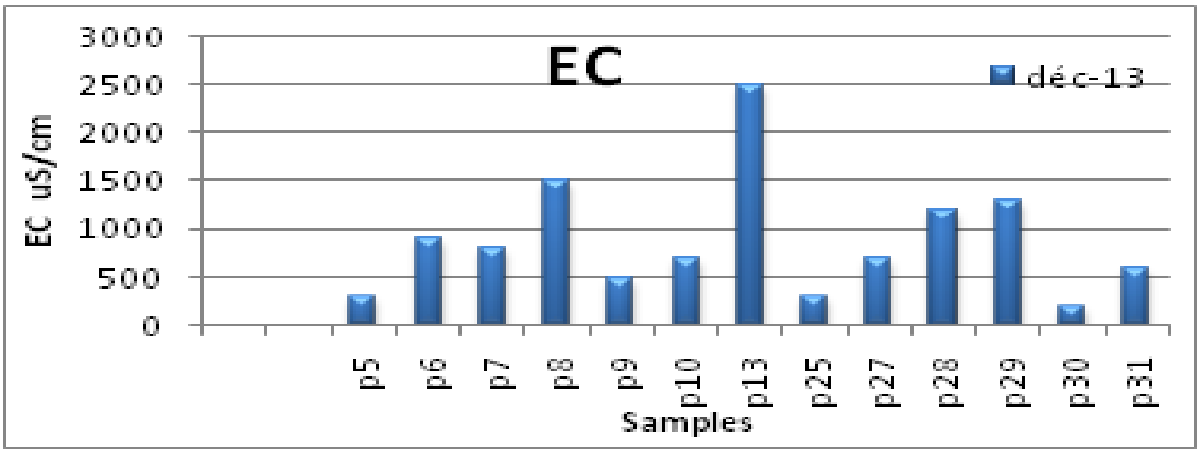

Fig. 3. Changes in the electrical conductivity (EC) of the groundwater.

The concentration of SO_4^{--} is higher, with an average of about 1973.12 mg/l; Cl^- ions are second with an average of 271.78 mg/l; the HCO_3^- are represented by an average of 332.11 mg/l, then the CO_3^{--} with 42.66 mg/l, followed by the NO_3^- with 29.49 mg/l and finally NO_2^- with 8.02 mg/l(Fig. 4). The total anion concentration is higher in the South and North Lake. The ranking of the anions according to their decreasing importance takes place in the following order:

$SO_4^{--} > Cl^- > HCO_3^- > CO_3^{--} > NO_3^- > NO_2^-$

For cations

The K^+ concentration is greater, with an average of about 460.33 mg/L; Na^+ is second with an average of 236.96 mg/l and Ca^{++} with an average of 45.11 mg/l, Mg^{++} with 37.73 mg/l and finally NH_4^+ with 9.06 mg/l (Fig. 5).

The classification of cations according to their decreasing importance takes place in the following order:

$K^+ > Na^+ > Ca^{++} > Mg^{++} > NH_4^+$

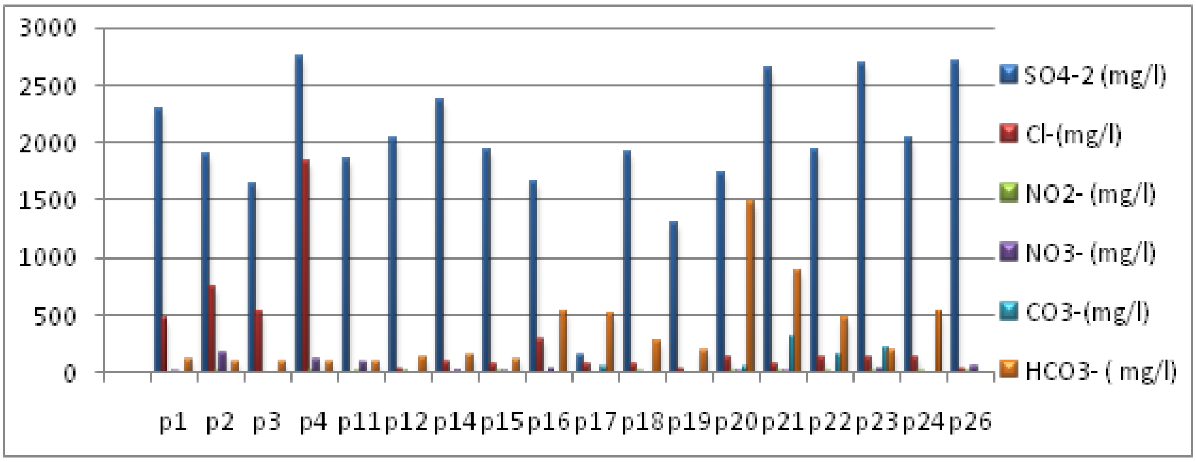

Fig. 4. The anion concentration of surface waters.

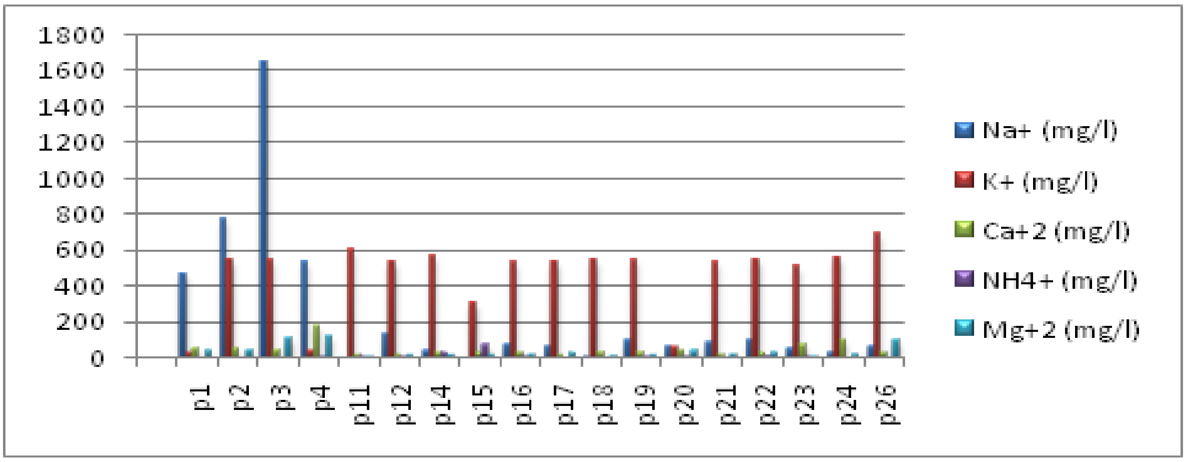

Fig. 5. The cation concentration of surface waters.

Ion concentration of Groundwater

SO_4^{--} is greater with an average of about 2011.16 mg/l; the HCO_3^- ions are second with an average of 190.50 mg/l, Cl^- are represented by an average of 155.43 mg/l NO_3^- then with 81.01 mg/l, followed by the CO_3^{--} with 16.61 mg/l and finally NO_2^- with 4.15 mg/l (Fig. 6).

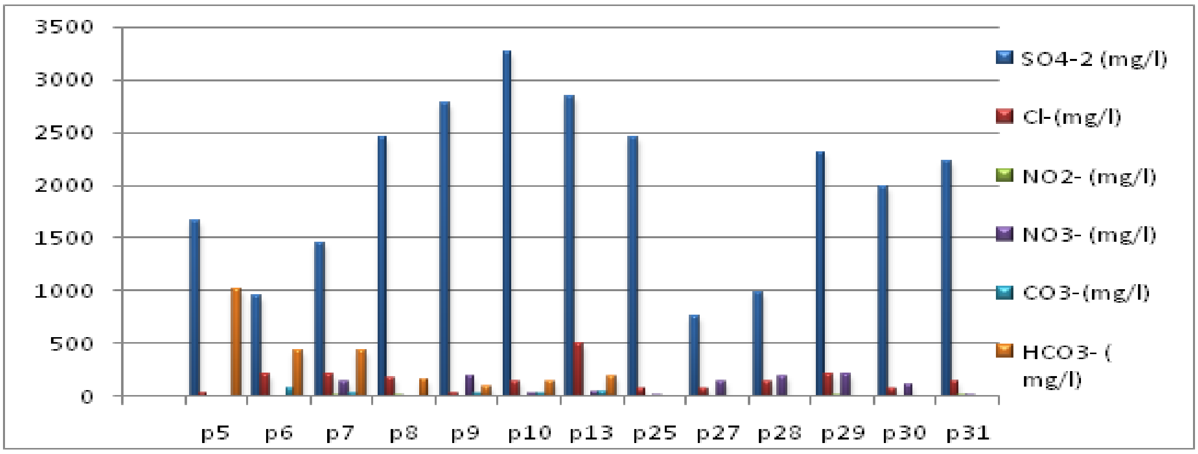

Fig. 6. The anion concentration of Groundwater.

The ranking of the anions according to their decreasing importance takes place in the following order:

$SO_4^{--} > HCO_3^- > Cl^- > NO_3^- > CO_3^{--} > NO_2^-$

Regarding the cation

The concentration of K^+ is always higher, with an average of about 461.07 mg/l, Ca^{++} arrives second with an average of 62.76 mg/l and Na^+ with an average 60.70 mg/l, then the Mg^{++} with 27.30 mg/l and finally NH_4^+ with 3.69 mg/l (Fig. 7).

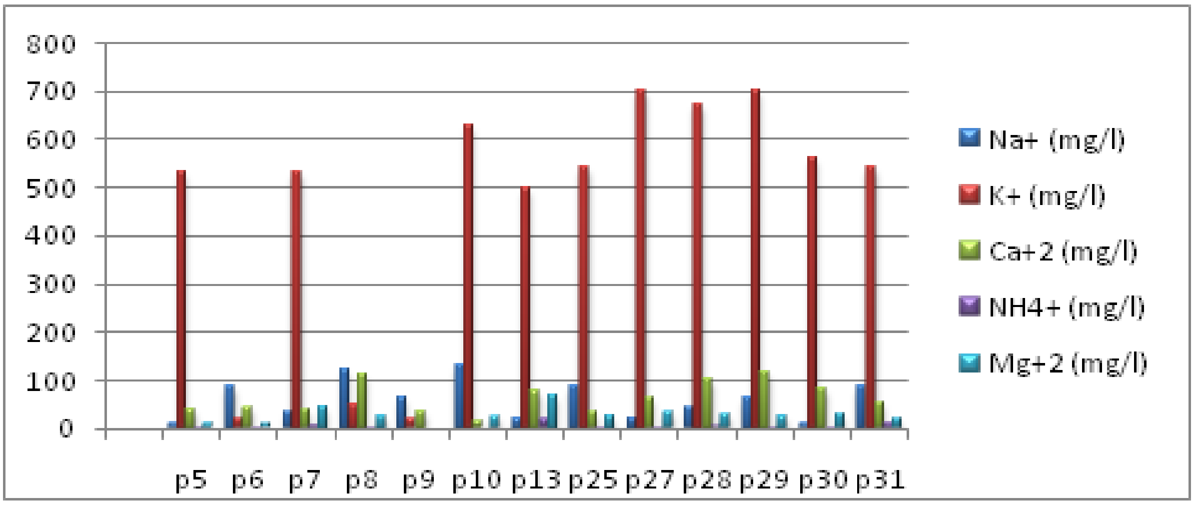

Fig. 7. The cation concentration of Groundwater.

The classification of cations according to their decreasing importance takes place in the following order:

$K^+ > Ca^{++} > Na^+ > Mg^{++} > NH_4^+$

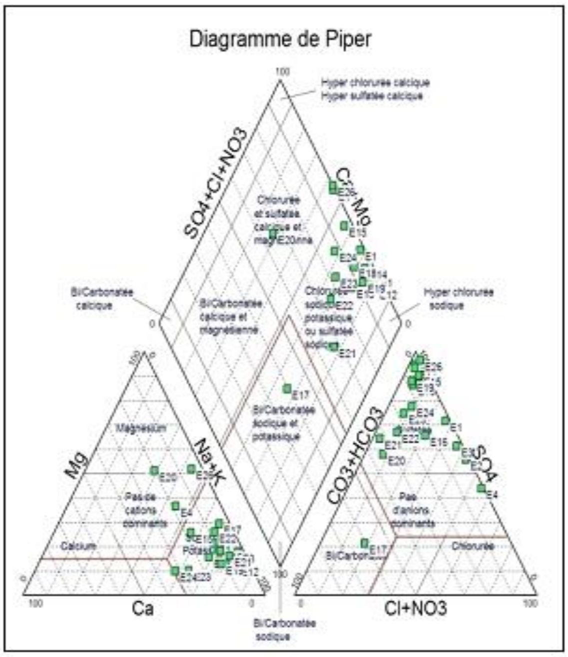

Fig. 8. Chemical facies of surface water (Piper diagram).

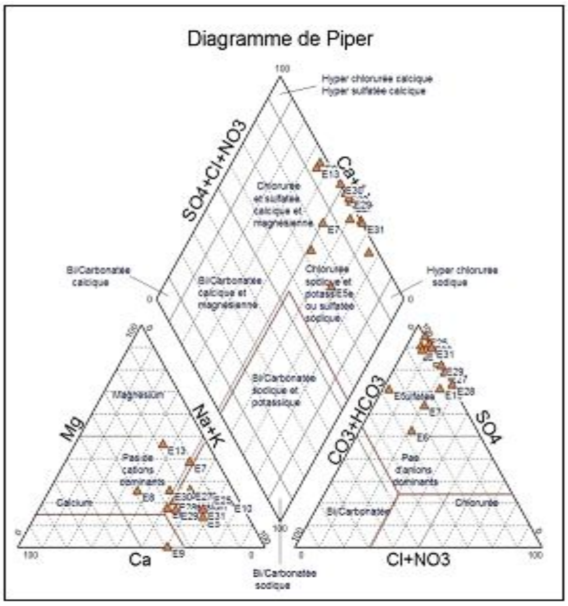

Fig. 9. Chemical facies of groundwater (Piper diagram).

Chemical facies

The Piper diagram shows a chlorated-sodic and potassic chemical facies with sodium sulfated, except a few samples that are bicarbonates sodium and potassium, so the sample P17 in El Eulma region (Fig. 8 & 9); the presence of these two elements (Na^+, SO_4^-) is due partly to the dissolution of evaporite formations rich in halite and also the contributions of licks Fetzara lake by the effect of evaporation (Djamai, 2007; Djamai *et al*, 2011).

Saturation index

Saturation indices are used to assess the degree of balance between water and mineral to highlight the different stages of the geochemical evolution of water that result in a change in these indices.

The indices of saturation obtained for the surface and underground waters are negative, all the samples have a sub- saturation to the calcite ($CaCO_3$) , anhydrite ($CaSO_4$) , halite (NaCl) , dolomite ($CaMg(CO_3)_2$) and gypsum ($CaSO_4 : 2H_2O$) . Therefore, a possible dissolution of these minerals can contribute to the acquisition of the salt content of the water , thus likely increasing mineralization (Fig. 10 & 11).

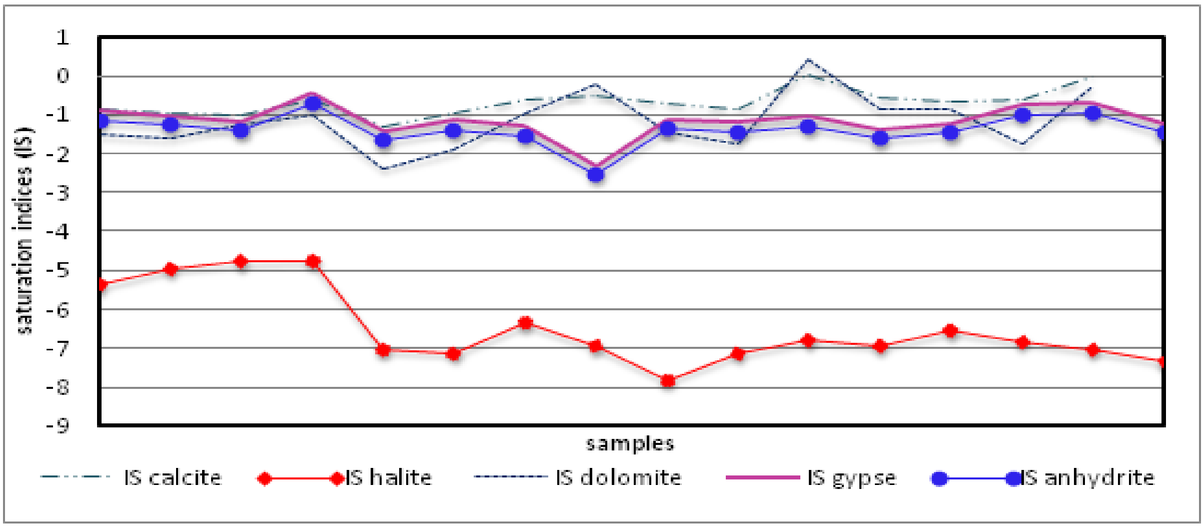

Fig. 10. Changes in indices of surface saturation (December 2013).

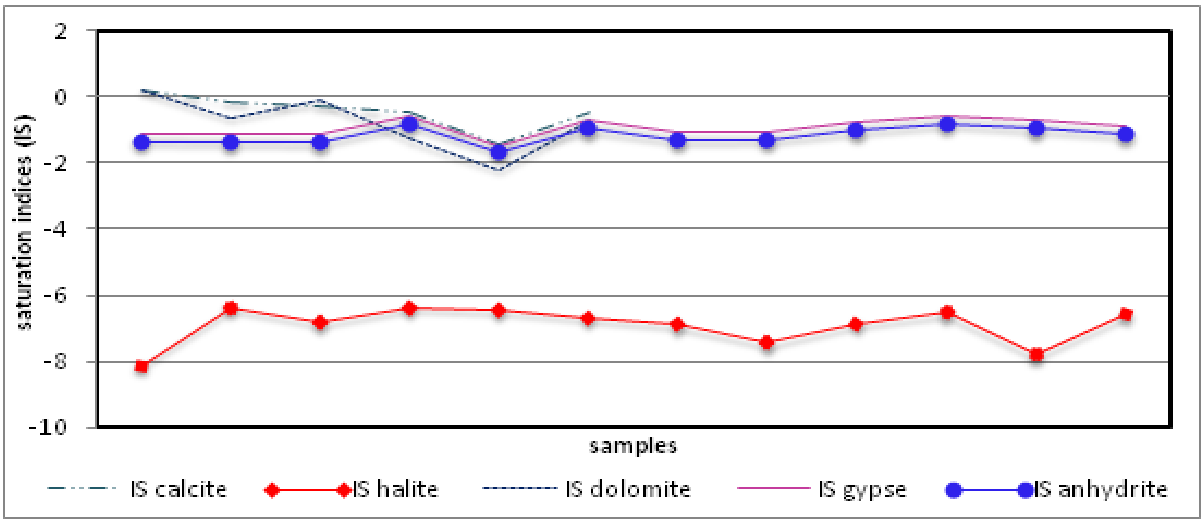

Fig. 11. Changes in groundwater saturation indices (December 2013).

Principal component analysis (PCA)

The purpose of this statistical analysis (PCA) is to bring out water points having high concentrations of chemical elements compared to other and identify associations that may exist. This will allow us to have an idea on the different elements and their origin.

We present in this study the projection of variables on the F1-F2 plane carrying a total inertia of approximately 56.77% for surface water and 51.14% for groundwater.

Factorial surface water

On the first axis, there is a resistance from the soluble salts are: SO_4^{--}, Cl^-, Na^+, Mg^{++}, NO_3^-, NO_2^-, Ca^{++} and EC representing the pole of the mineralization front the HCO_3^-, K^+, CO_3^{--} and pH, located in the negative part (Fig. 12).

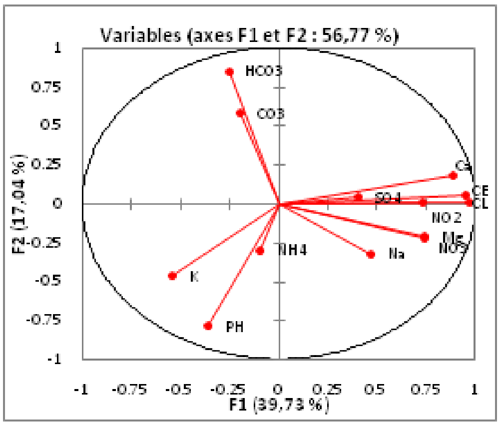

Fig. 12. Principal components analyzes of lake surface water Fetzara.

In terms of individuals, it is the P3 sample that is a secondary channel connected to the main channel, which has highly mineralized water (Fig. 13), this opposition is explained by the water salinization process under the effect of evaporation is a very common natural process in the Maghreb.

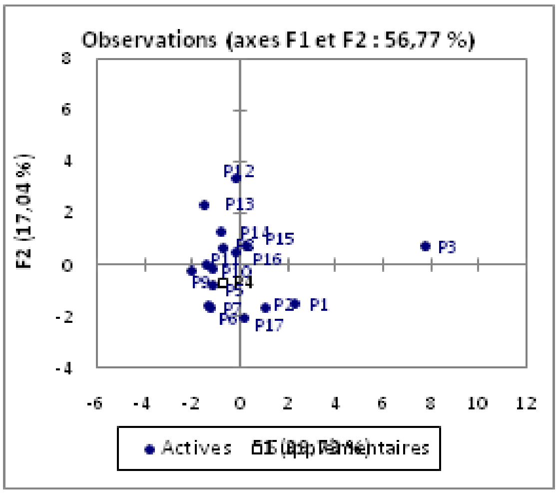

Fig. 13. Contribution of different individuals of surface water from Lake Fetzara.

In the second factorial axis, we also note a contrast between HCO_3^- CO_3^{--} in the positive pole and the other NH_4^+, K^+ and pH. In terms of individual samples P12, P13, P14 and P15 have the carbonated waters in the town of Cheurfa. This probably reflects phenomena oxidation - reduction.

Factorial groundwater

The first factor axis indicates a positive pole of the main mineralization soluble salts are NH_4^+, CO_3^{--}, Cl^-, Mg^{++}, and HCO_3^- EC, opposite the nitrogen ions NO_3^-. In the negative, in terms of individuals, the samples P1, P2, P6 and P7 have highly mineralized waters are waters Cheurfa, subject to the effect of high evaporation in the dry season (Fig. 14).

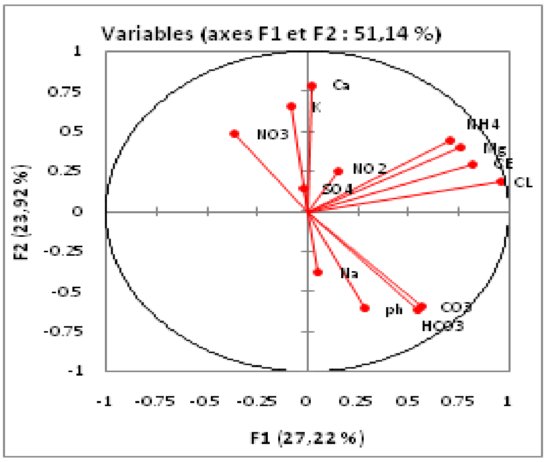

Fig. 14. Principal components analyzes of ground water from Lake Fetzara.

In the second factorial axis, there is a contrast between on the one hand NO_3^-, K^+, Ca^{++} in the positive pole and the other CO_3^{--}, HCO_3^- and pH .. In terms of individual samples P7, P9 , P10, P11 and P12 have the carbonated water in the town of Cheurfa. This probably reflects phenomena oxidation - reduction (Fig. 15).

Nitrates and soluble salts correlation

Two thirds of the nitrates pollution caused by agricultural activities and intensive farming (Debieche, 2002). Nitrates interactions and soluble salts show the degrees of correlation between these elements (Table 1).

Correlation nitrate/chloride

The nitrates and chlorides relationship in surface waters appears strong with a correlation coefficient R2 = 0.70 for the points P1, P2, P3 and P4, this last has the highest value 1843.4 mg/l of chloride and 116.62 mg/l nitrates in the region of El Gantra (Fig. 16). This area is surrounded by bare land, where the nitrate migration is significantly faster on arable land during the winter (Enfield *et al.*, 1990).

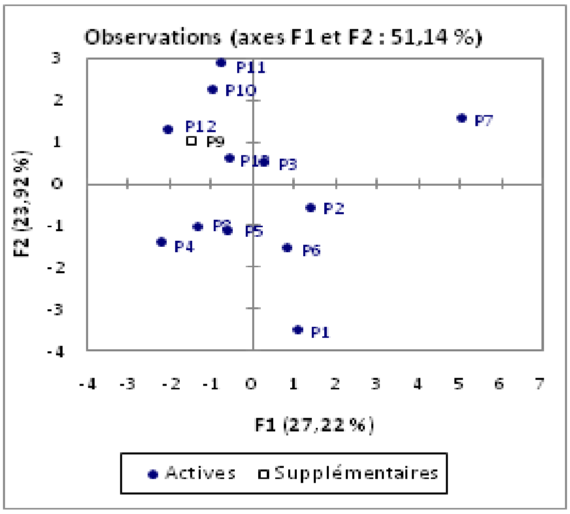

Fig. 15. Contribution of different individuals ground water Lake Fetzara.

In groundwater that relationship is weak (R2 = -0.22) with concentrations of chloride lower compared to those of surface waters, where they reach a maximum of 496.3 mg/l only because the soluble salts in the dry season are to the ground surface due to the absence of precipitation leading to the groundwater.

Correlation nitrate/nitrite and electrical conductivity

In surface waters, nitrate relationship and electrical conductivity is high with a correlation coefficient R2 = 0.65 and R2 = 0.64 nitrites especially for P2 and P4 points. It is noted that when the electrical conductivity increases, the values of nitrates undergo an increase. P4 represents the most important values, they manage to 7500 µS/cm electrical conductivity and 166.62 mg/l for nitrates. These are rivers into Lake Fetzara (Fig. 16). Nitrates are positively correlated with salinity and nitrites which are rapidly converted into nitrates. In groundwater this relationship remained significant with nitrites (R2 = 0.41), with low electrical conductivity (R2 = -0.10), due to climatic factors particularly the lack of rainfall.

Correlation nitrate/calcium and magnesium

The relationship of nitrate calcium and magnesium of Lake Fetzara surface water, remains positive with a correlation coefficient R2 = 0.50 with calcium and R2 = 0.46 with magnesium. The P4 sample remains the one with the highest levels with 176.35 mg/l for calcium and 126.36 mg/l for magnesium is the nearest secondary channel from the center of Lake Fetzara, which is most affected by the phenomenon of evaporation during the dry period (Fig. 16). In groundwater, this relationship remained significant with calcium (R2 = 0.35), with low magnesium (R2 = -0.12).

Correlation nitrate/sulfates and sodium

In surface waters of Lake Fetzara the relationship nitrates sulfates and sodium nitrate is not very significant. The correlation coefficient with sulfates is 0.32 and 0.30 for sodium; Samples P2 and P4 in the lake Fetzara are those with the highest levels with 2738.67 mg/l for sulfates and 538.89 mg/l for sodium in the point P4 (Fig. 16). In groundwater that relationship is weak to the sodium (R2 = -0.31) and sulfates (-0.13), as soluble salts in the dry season remain in the soil surface.

Correlation nitrates/other chemical elements

The relationship nitrates with other chemical elements is low with coefficients of negative correlations, it is the case of potassium, carbonates, bicarbonates, pH and ammonium ions, this is due to lack of these ions leaching to groundwater in the dry season and the uptake of these ions by plants at the surface water.

Ability of water for irrigation

SAR (sodium absorption ratio) is used in conjunction with electrical conductivity; report results on Richards diagram classifies different types of irrigation water and indicate their use.

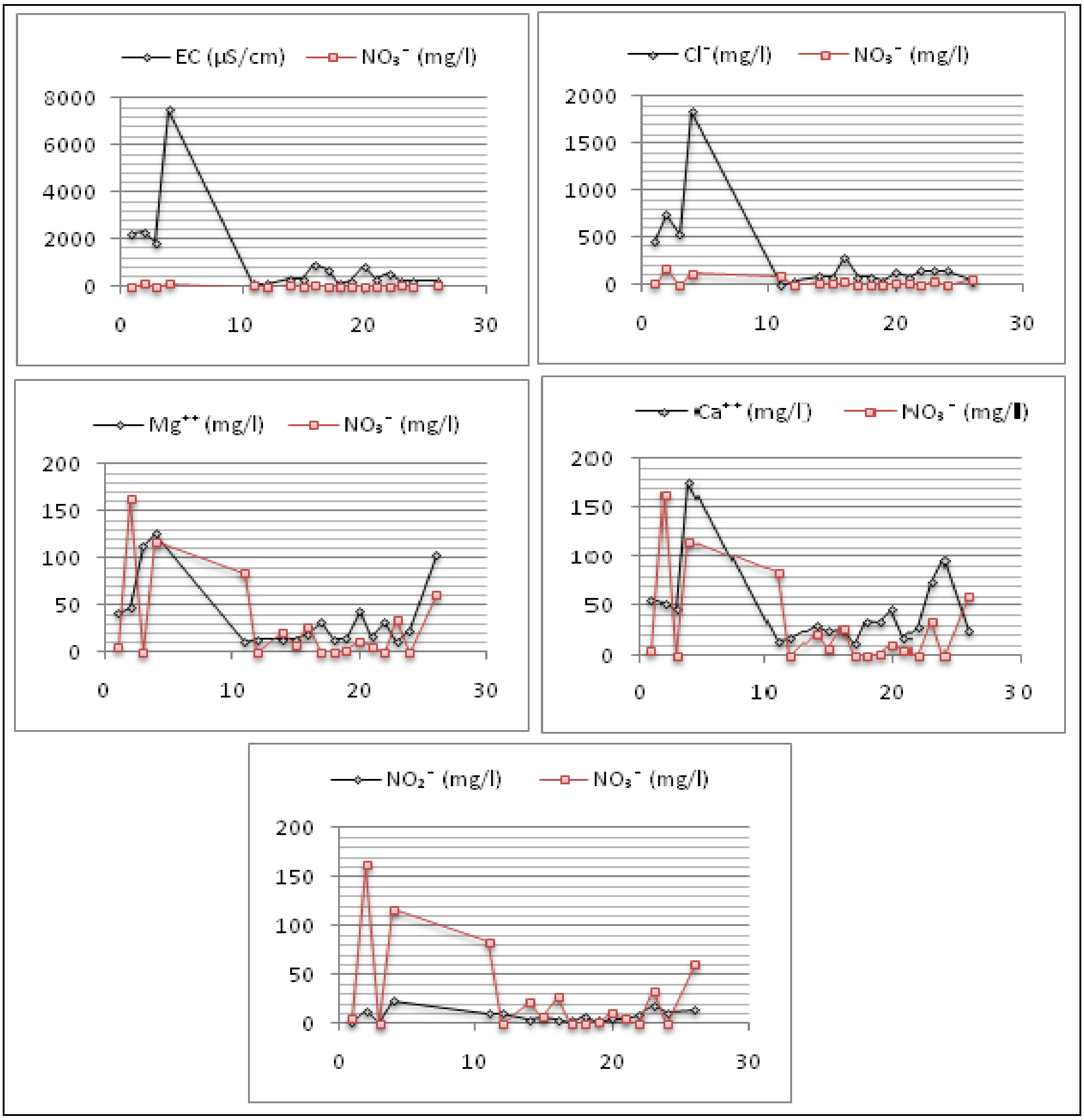

Fig. 16. Correlation nitrates and main chemical elements for surface water.

$$SAR = \frac{Na+}{(\sqrt{Ca^{++}}+\sqrt{Mg^{++}})/2}$$

Sodium, calcium and magnesium are expressed in mg/l. Richards diagram applied to waters of Lake Fetzara, brings up three classes of water: good, eligible and poor (Fig.17 &18).

Good (C1S1-C2S1): water that can be used without special control for irrigation of most crops on most soils. This category is present at surface water with twelve (12) samples and seven (07) for groundwater.

Eligible (C3S1-C3S2): water suitable for irrigating crops tolerant salts on well-drained soils. This class represents the majority of samples and is located to the northeast and southeast of the lake near Cheurfa.

Poor (C3S3-C4S1): highly mineralized water to suit the irrigation of some species much salt tolerant and well-drained and leached soils.

These poor quality of water occupy the secondary channel (P1) and the well (P13) located in the southeast of the lake.

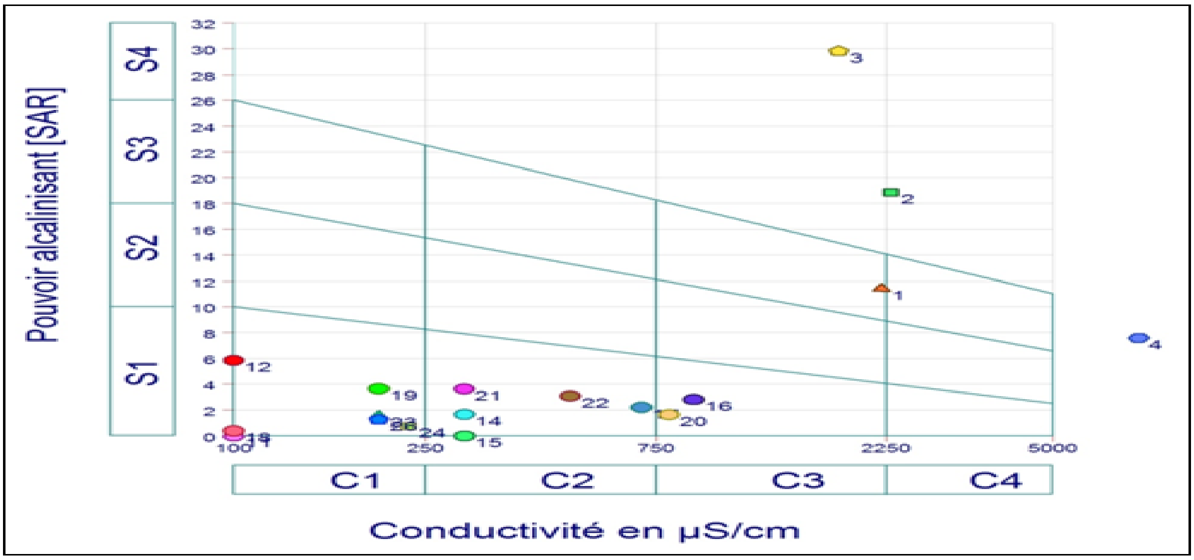

Fig. 17. Classification of surface waters according Richards diagram.

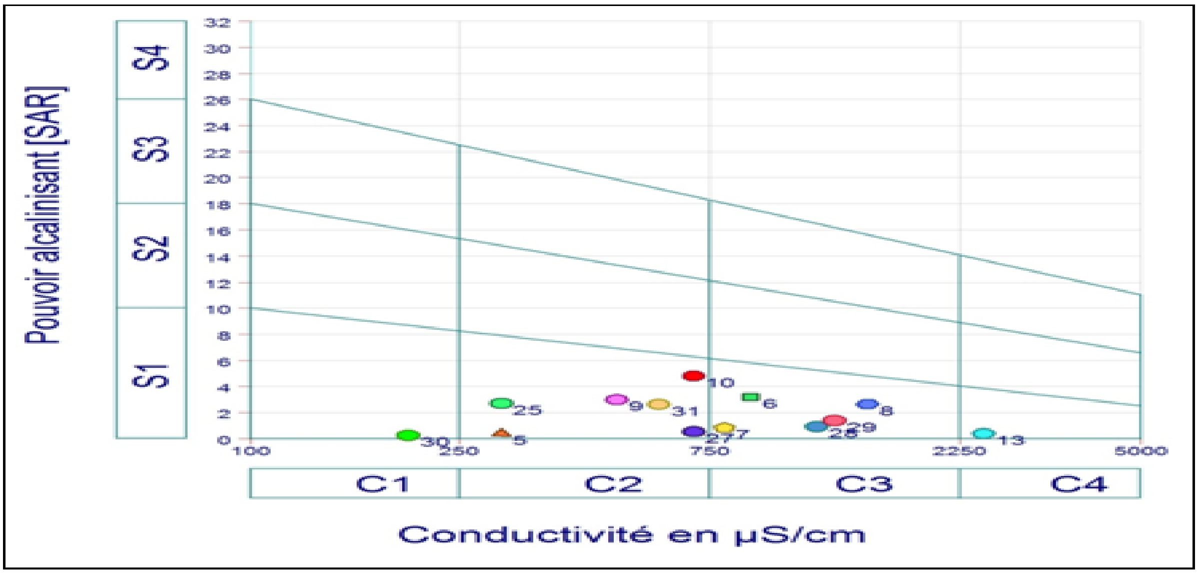

Fig. 18. Classification of groundwater by Richards diagram.

Conclusion

Geochemical study of surface and ground waters of Lake Fetzara has shown a high salinity.

This mineralization is particularly important in surface water due to the presence of certain elements in high concentrations (NO_3^-, Ca^{++}, Na^+, SO_4^{--}, Cl^-).

These waters are characterized by a chemical facies chlorated-sodium and potassium to sodium sulfated. The study of the relationship between the nitrates and various other soluble chemical elements has shown that there is a connection which positively moves between the nitrates and chlorides, electrical conductivity, nitrites, calcium, magnesium, sodium and sulfates.

The high concentration of nitrates in surface waters is mainly due to the use of fertilizers on the agricultural area and the contribution by rainwater and runoff.

In groundwater this relationship is positive only with nitrite, potassium and calcium.

These results were confirmed by principal component analysis (PCA).

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