INNSPUB

Journal of Biodiversity and Environmental Sciences (JBES)
ISSN: 2220-6663 (Print) 2222-3045 (Online)
Vol. 13, No. 3, p. 7-16, 2018
http://www.innspub.net

RESEARCH PAPER OPEN ACCESS

Geochemistry and empirical, graphical and statistical classification of waters of an ecosystem Lacustrian: classification of humid zone Case Fetzara Lake (North-East Algeria)

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Article published on November 15, 2018

Key words: Fetzara Lake, Geochemistry, PCA, AHC, salinity.

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. This study objective is to determine the physico-chemical characteristics and the classification of the Fetzara lake's water (North-eastern Algeria) by using the characteristic reports of major elements, Piper diagram, the analysis of the matrix of correlation, the ascendant hierarchic classification (AHC) and the principal component analysis (PCA). The results allow us to classify statistically the Fetzara lake's water into 4 distinct groups: the first group of high salinity are waters of the South- East region of the lake, the second one of an excessive salinity situated in the center of the lake, the third one of average salinity characterize the North-East of the lake and the last one of sulfate waters of high salinity in the south of the fetzara lake.

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Introduction

Resources in ground water around the Mediterranean, particularly those of the Middle East and North Africa, are experiencing increasingly quantitative and qualitative degradation (custodio et bruggeman, 1987; edmunds et droubi, 1998 ; vengosh et rosentha, 1994, ; vengosh *et al*,1999).

The North of Africa is typically a semi-arid region where water resources are susceptible to develop under the influence of climatic fluctuation where the human action exists (Cudennec *et al*, 2007). These changes can affect the stocks of groundwater which are rarely in increase (Idder, 2007), and those which are often in considerable decrease (bouhalassa *et al*, 2008).

The salinity of water presents one of the big problems in Algeria, view its devastating effect on the quality of water. It is often related to the dissolution of the geologic formations, under evaporation effect and under probable sea intrusion effect. The Fetzara lake has been classified like it was a humid zone protected the 4th of June 2003 by the RAMSAR convention, the salinity of the water and the soil's lake has made the object of a good number of works (Durant, 1950; ifagraria, 1967; A.J.C.I, 1985; djamai, 1993, 2007 et 2011; zenati, 1999 ; belhamra, 2001 ; habes, 2006 et 2013 ; zahi, 2008 et 2014 ; laouar *et al*, 2002; fekrache, 2015). Our study takes under the characterization and the classification of the lake's water by the empirical graphical and statistic techniques to know the study of characteristic reports, the principal component analysis and the hierarchic classification analysis.

Geographic situation

The Fetzara lake is situated in the North-East of Algeria, it is found 18 km in the South-West of Annaba city. It is stretched out at 17 km from the East to the West and at 13 km from the North to the South with a surface area of about 20.680 ha .The lake is limited in the North by the head's area of the municipal of Berrahal, in the South by the territories of El Eulma's municipals and El Cheurfa and in the East the small villages of El Gantra and Oued Zied (fig. 1). In the hydrologic plan, the flow of water in the region of the fetzara lake are characterized by a very irregular regime, torrential in the winter and dry in the summer.

The networks in the superfial water are constituted by a ramification of free areas; the beds of these flows of water are widened in the downhill parties that are in the contact of the lake.

Oued EL Hout in the South, Oued Melah in the West and Oued Zied in the North East are the principal Ouedi that supply the Fetzara lake, and Oued Meboudja that assure the drainage of the lake's water.

This region is submissive to a Mediterranean climate characterized by two distinct seasons, one is fresh and humid, the other is hot and dry.

And another one which is dry and hot with an annual average precipitation between 670.8-633.9 mm and annual average temperatures that vary from 11.44-25.56 c°.

Materials and Methods

The period of sampling took place in May 2014 for a total of 25 samples, related to surface water (15 samples) and groundwater (11 samples), on the edge of the Fetzara lake (Fig. 2).

The analysis of chemical elements was performed according to standard analytical methods (Rodier *et al*., 1978 and 2009): Chloride (Cl^-), carbonates (CO_3^{--}) and Bicarbonate (HCO_3^-) by titration (Mohr method) ; Sulfates (SO_4^{--}), Nitrite (NO_2^-) , Nitrate (NO_3^-) and ammonium (NH_4^+) by spectrophotometry; Calcium (Ca^{++}) and Magnesium (Mg^{++}) by complex metric EDTA; Sodium (Na^+) and Potassium (K^+) by spectrophotometry at flame.

For this study, we have used the characteristic reports such as the principal component analysis (PCA) and the Ascendant Hierarchic Classification (AHC) excel stat 2015.

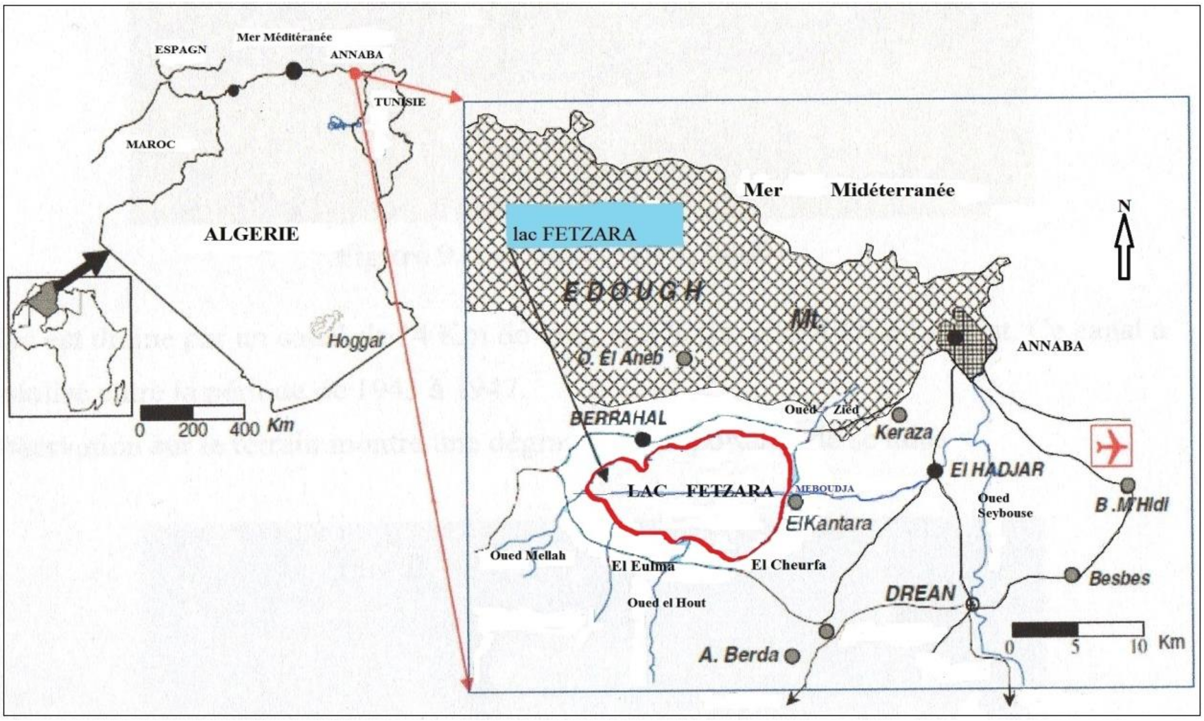


Fig. 1. Geographical Situation of the Fetzara Lake.

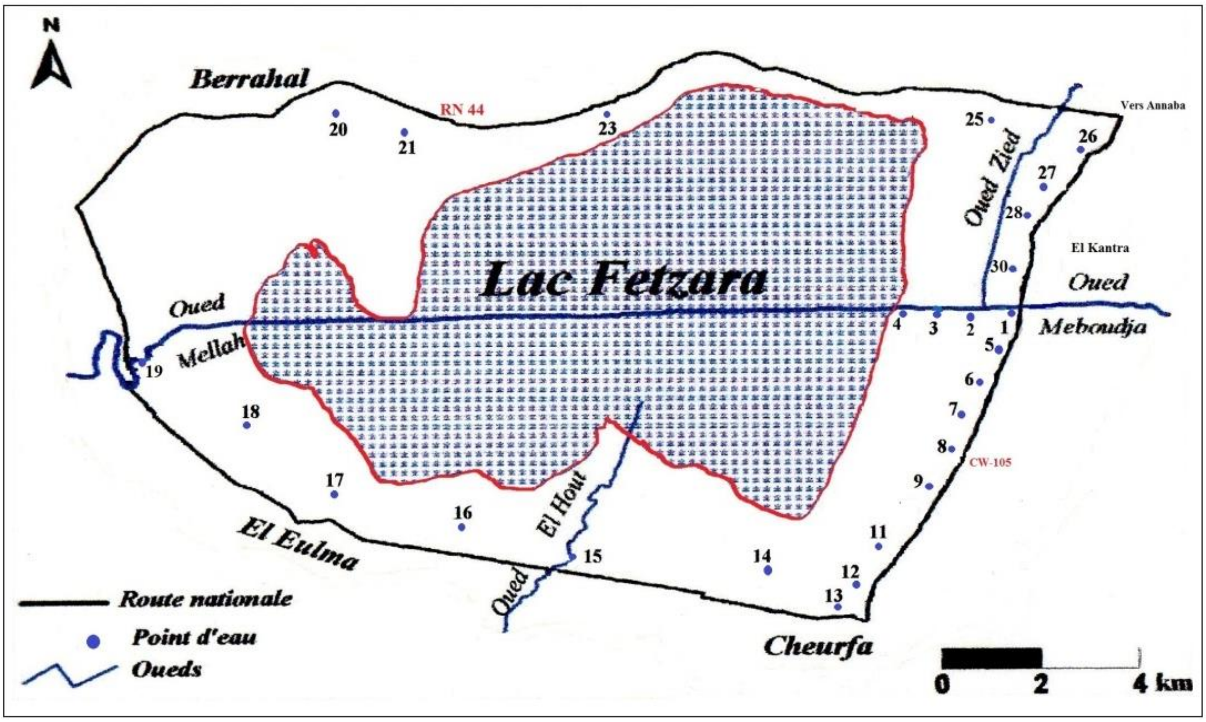


Fig. 2. Inventory Map of Sampling Points.

Results and discussion

Geochemistry of the Lake's Water

The statistic descriptive parameters of an average position, dispersion (minimum, maximum and deviation type) of major cations and anions of the Fetzara lake's water (Table 1).

Characteristics reports

Na^+/K^+

The Na + / K + is of the order of 47 for sea water and less than 10 for rainwater(Alayat *et al*, 2007), This report shares the lake into two groups: the first group with a ratio greater than 47 represents the majority of samples, and the second group with reports Na + / K + between 10 and 47, So an intermediate quality between fresh water and sea water were the waters of Cheurfa region southeast of Lake Fetzara (fig. 3).

Table 1. Descriptive Statistics of Chemical Elements of the Fetzara Lake.

Variable (meq/l)	Minimum	Maximum	Average	déviation-type
Cl^-(meq/l)	2,000	69,000	12,037	12,361
Na^+(meq/l	4,780	57,390	16,228	10,217
K^+(meq/l	0,020	0,510	0,171	0,117
Ca^{2+} (meq/l	0,400	4,280	1,176	0,799
Mg^{2+} (meq/l	1,280	6,240	3,283	0,988
HCO_3^-(meq/l	4,400	36,800	22,341	7,907
SO_4^{2-} (meq/l	1,380	46,250	22,910	11,365
EC (uS/cm)	640,000	6090,000	1712,963	1020,471
TDS	1434,000	5825,000	3457,370	929,671

Table 2. Na^+/Cl^- reports, indices of basic exchanges (IBE) and saturation indice (SI).

	Samples	Na^+/Cl^-	IBE	IS calcite	IS dolomite
	1	1.58	-0.59	0.12	0.9
Surface water	2	1.18	-0.19	0.35	1.32
	3	1.30	-0.31	0.56	1.32
	4	0.83	-0.16	1.6	3.41
	5	0.96	0.018	0.04	1.16
Groundwater	6	2.93	-1.98	0.81	2.41
	7	1.42	-0.45	0.59	2.04
	8	3.47	-2.61	0.2	0.77
	9	1.19	-0.25	0.22	1.07
Surface water	11	1.66	-0.68	-0.78	2.15
	12	1.07	-0.10	0.13	0.73
Groundwater	13	1.77	-0.78	-0.16	0.73
	14	0.97	0.009	0.37	1.14
	15	1.02	-0.038	0.34	1.43
	17	2.08	-1.10	0.19	1.27
	18	1.66	-0.67	0.63	1.96
Surface water	19	2.60	-1.61	0.43	1.53
	20	1.61	-0.67	0.24	0.94
	21	1.47	-0.48	0.26	1.28
	23	2.10	-1.10	0.56	1.84
groundwater	25	1.73	-0.74	0.73	2.14
Surface water	26	1.65	-0.70	-0.006	0.18
	27	1.21	-0.22	0.48	1.14
groundwater	28	3.47	-2.49	0.59	1.79
	30	1.42	-0.46	0.83	2.14

Na^+/Cl^-

Na^+/Cl^- report allows the classification of the lake's waters in one group (fig.4), where the points show reports similar to 1 and indices of basic exchanges (IBE) very weak. What plaids in faveur of a halite dissolution (Table 2).

Ca^{+2}/Mg^{+2} et Ca^{+2}/SO_4^{-2}

All the water's lake present a report of Ca^{+2}/Mg^{+2} inferior to 1, the fact that signifies that magnesium take away calcium (fig.5). The evaporated origin of magnesium is strong, calcium comes from the dissolution of calcite and of gypsum as the report confirms Ca^{+2}/SO_4^{-2} (fig.6).

$(Ca^{+2} + Mg^{+2})/HCO_3^-$

The report $(Ca^{+2} + Mg^{+2})/HCO_3^-$ show an excess of HCO_3^- where all of the points situated above the first slope on the right 1. Ionic concentration of HCO_3^- is stronger than the ions Ca^{+2} and Mg^{+2} (fig. 7).

Table 3. Correlation matrix between physico-chemical parameters.

	Cl	Na^+	K^+	Ca^{2+}	Mg^{2+}	HCO_3^-	SO_4^{2-}	C.E
Cl^-	1							
Na^+	0,91	1						
K^+	0,02	-0,11	1					
Ca^{2+}	0,69	0,54	0,04	1				
Mg^{2+}	0,35	0,40	-0,14	0,37	1			
HCO_3^-	-0,42	-0,43	0,21	-0,36	0,15	1		
SO_4^{2-}	0,23	0,33	-0,38	0,17	0,40	-0,059	1	
EC	0,94	0,92	0,001	0,68	0,50	-0,314	0,394	1

$[(Ca^{2+} + Mg^{2+}) / (SO_4^{-2} + HCO_3^-)]/ Na^+/Cl^-$

The graphic representation of $SO_4^{-2} + HCO_3^-$ of a $(Ca^{+2} + Mg^{+2})$ function indicates that the points are divided around the 1 slope on the right, the fact that the principal geochemical phenomena intervene in general in the acquisition of saline load are related to the interaction of a crystal (dissolution and precipitation of minerals: calcite, dolomite, gypsum, anhydrite and basic exchanges with clayish minerals) (Fig.8).

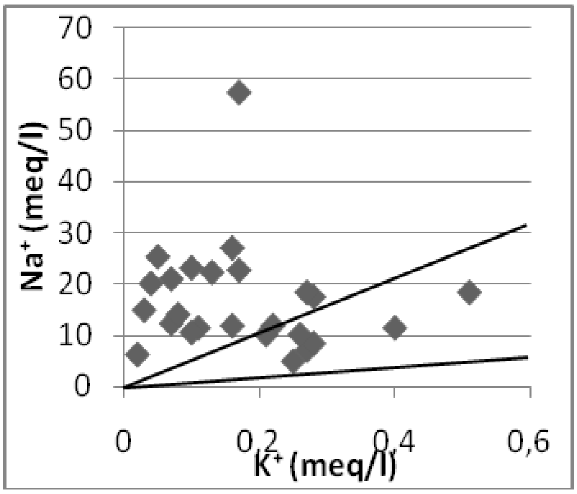


Fig. 3. Report Na^+/K^+.

Piper diagram

We observe the dominance of chemical faciés which are sodic chloride and potassic of a sodic sulfate except some samples of cheurfa region that are potassic and sodic bicarbonates (fig.9). The sodic chloride faciés and potassic are frequently in environments full of evaporate (example halite) and the sodic carbonate faciés and potassic are found in certain aquifers of the sedimentary basin and show the crystal interaction (Ca^{++}exchange against Na^+ at clays) (Bourhane, 2010).

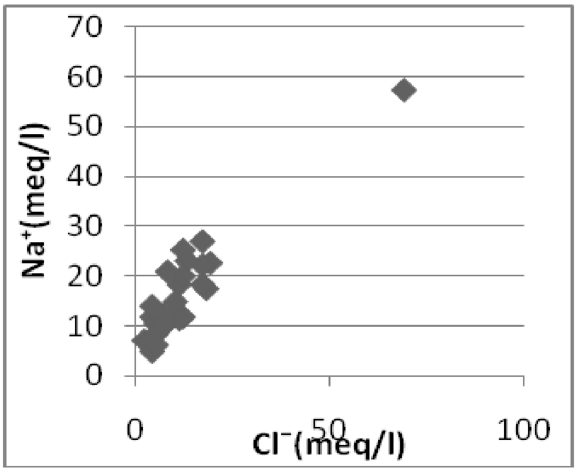
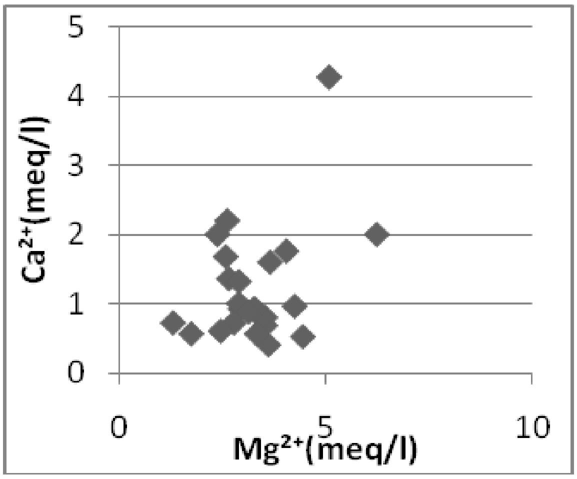


Fig. 4. Report Na^+/Cl^-



ig. 5. Report Ca^{+2}/Mg^{+2}.

Statistical analysis

For 25 points all 08 variables and the threshold 05%, the weight of critical correlation is r= 0.50, on this basis (Table 3), various significant correlations could be identified and have allowed to show the best correlation group: Na^+, Cl^-, Ca^{2+}.

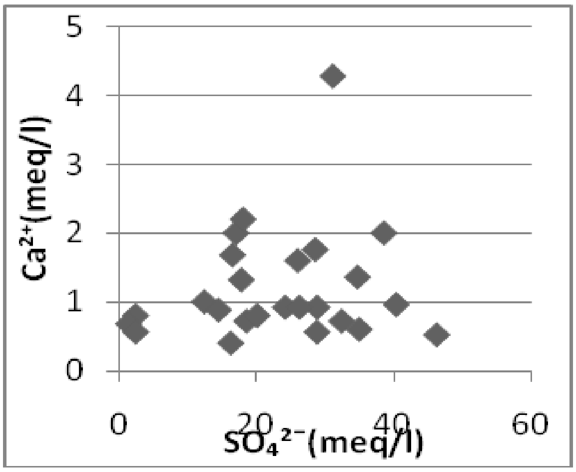


Fig. 6. Report Ca^{+2}/SO_4^{-2}

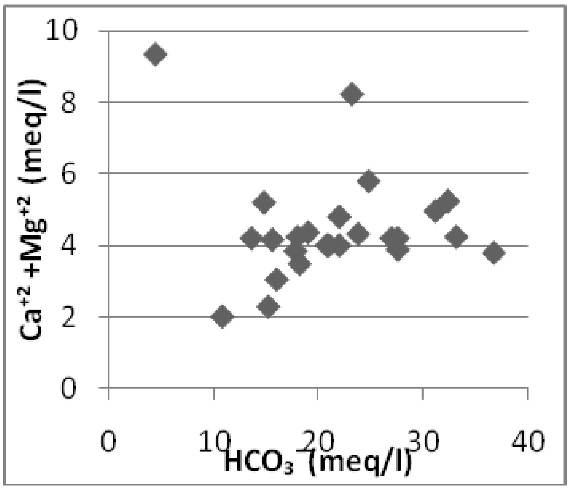


Fig.7 . Report $(Ca^{+2} + Mg^{+2})/HCO_3^-$

These significant links can be attributed to communal origins of these elements (the dissolution of evaporated saliferous formations).

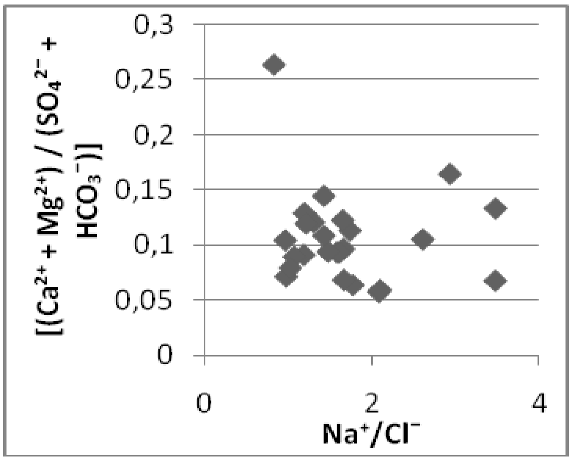


Fig. 8. Report $[(Ca^{+2} + Mg^{+2})/(SO_4^{-2} + HCO_3^-)]/Na^+/Cl^-$.

No significant correlation threshold to 5% has not been observed between magnesium and the other chemicals elements. We also note that no significant link was observed between HCO_3^- and SO_4^{2-}.

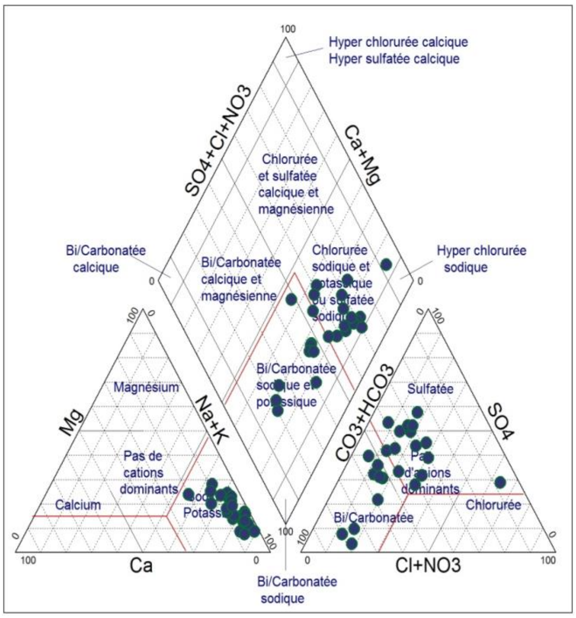


Fig.9. Piper diagram of Fetzara lake's waters (May 2014).

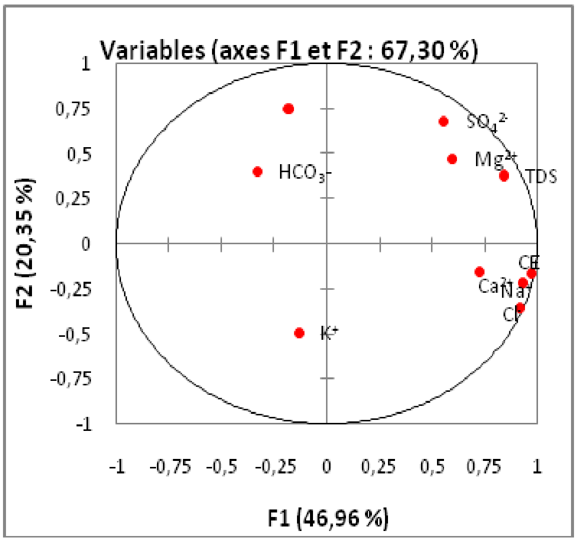


Fig. 10. Projection of variables.

This suggests that these two ions are involved in distinct geochemical processes.

The other chemical quantities contribute considerably to the conductivity of the water's lake. This conductivity is related essentially to chlorides and sodium.

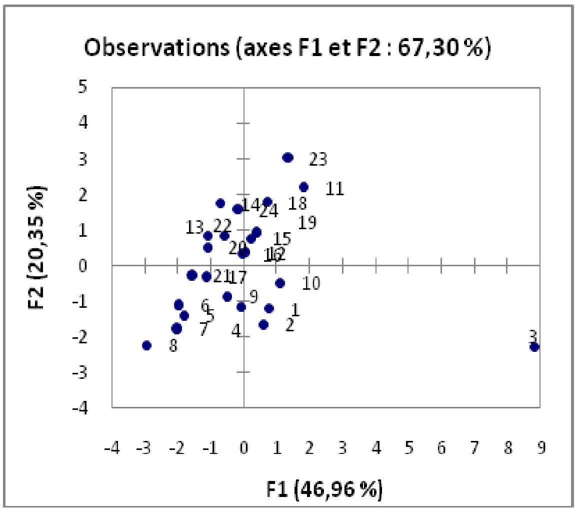


Fig. 11. Projection of individuals.

Principal component analysis (PCA)

The projection of variables on the plan 1-2 shows that 1 axe expresses 67.30 % of variance and oppose the soluble salty principles that are: SO_4^{--} , Cl^-, Na^+, Mg^{2+}, Ca^{2+} et CE and this is the same sample P3 that presents the strong mineralization of the waters. This also that the waters are strongly mineralized in a wintry period. The climate has played certainly a crucial role for loading of waters with rainfalls and runoff (fig.10).

In the second factorial axe, we observe an opposition between HCO_3^- in the positive pole and the other part of K^+. In the plan of individuals, the samples: P11, P18, P23, P14 present carbonate waters, these are the cheurfa communal waters and El Eulma (fig.11).

This probably translated oxydo- reduction phenomena and may be a fixation of ions by clayish minerals. Particularly that these soils allomorphic in the eastern and south eastern parties of the lake, characterized by the presence of soluble salts, a dense texture which is full of blowing clayish minerals.

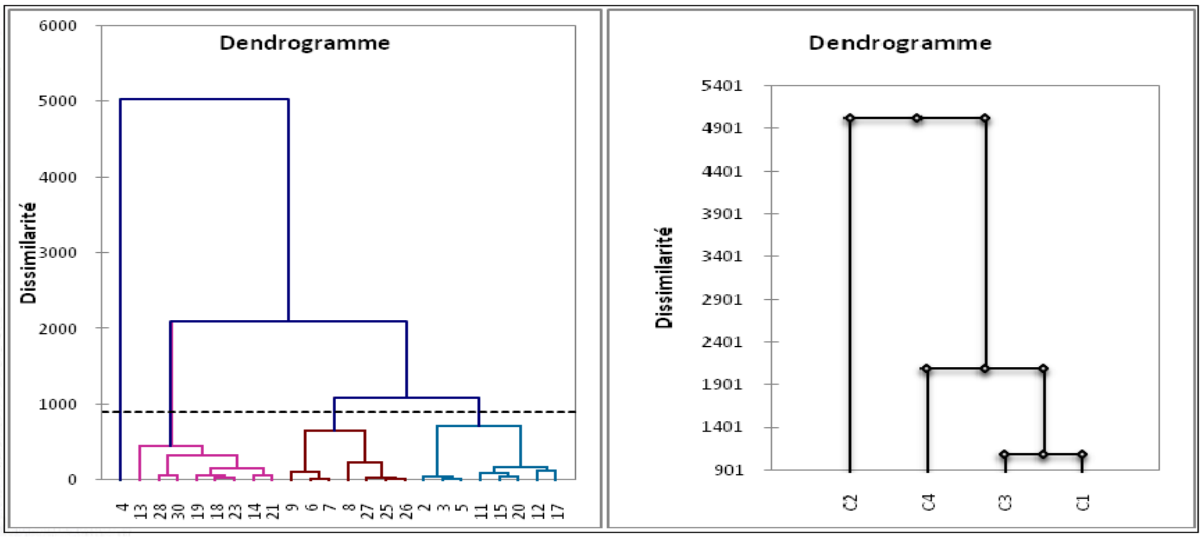


Fig. 12. Dendogram of hierarchic classification.

Ascendant Hierarchic Classification (AHC)

Figure 12 illustrates the dendogram of the hierarchic classification of the Fetzara lake's water which show the existence of 4 groups: the first one represents the class of high salinity, the second group is the one of excessive salinity, the third one is between average and high salinity like the first group but with much higher sulfate concentrations.

Conclusion

The empirical multivariable classification, statistic and graphical of the lake's waters allow to give a methodology of classification permitting to take the advantages of each technique, and permitting for example a multivariable classification of the lake's waters by conserving the facility of graphical representations of the chemical interpretations of waters. In that way, this combining has allowed to classify the waters statistically into distinct 4 groups: the first group waters of high salinity belongs to the south eastern region of the lake, the second group of excessive salinity situated in the centre of the lake, the third one of average salinity characterize the north-east of the lake and the last one sulfate waters of high salinity in the southern region of the lake.

The chemical analysis of the Fetzara lake's waters show that these waters present considerable concentrations of chlorides, sulfates, sodium, potassium, bicarbonates.

The exploitation of characteristic reports and the Piper diagram demonstrate that the lake's waters are in majority sodic chloride of sulfate potassic sodic. These characteristic reports divides waters in 3 groups on the basis of : the mentioned report : Na^+/K^+ and $[(Ca^{2+} + Mg^{2+})/(SO_4^{-2} + HCO_3^-)]/Na^+/Cl^-$ .this can be explained by the crystal interaction particularly in the wintry seasons and the basic exchanges of clayish minerals.

Acknowledgements
I want to thank the entire staff of the Biology Department and in particular those laboratories, écopédologie and Plant Physiology and Plant Biology Research and Ecology and Environment has Badji Mokhtar Annaba University , Mr Hazourli teacher at the Department of Biochemistry Badji Mokhtar Annaba 's University Many thanks to Mr Benadouda Faouzi and Mme Mitidji Houria for the physical and moral support.

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