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Hydrochemical characterisation of groundwater using multifactorial approach in Foum el Gueiss basin, Northeastern Algeria

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Abstract: Knowledge of the quantity and quality of groundwater is a prerequisite to encourage investment in the development of a region and to consider the sedentarisation of populations. This work synthesises and analyses data concerning the chemical quality of the available water acquired in the Foum el Gueiss catchment area in the Aures massif. Two families of waters are observed, on the one hand, calcium and magnesian chlorated-sulphate waters and on the other hand, calcium and magnesium bicarbonate waters. Multivariate statistical treatments (Principal Component Analysis – PCA and Discriminant Analysis – DA) highlight a gradient of minerality of the waters from upstream to downstream, mainly attributed to the impact of climate, and pollution of agricultural origin rather localised in the lower zones. These differences in chemical composition make it possible to differentiate spring, well and borehole waters. The main confusion is between wells and boreholes, which is understandable because they are adjacent groundwater, rather in the lower part of the catchment area. The confusion matrix on the dataset shows a complete discrimination with a 100% success rate. There is a real difference between spring water and other samples, while the difference between wells and boreholes is smaller. The confusion matrix for the cross-validation (50%).

Keywords: discriminant analysis, Foum El Gueiss, groundwater quality, hydrochemistry, irrigated agriculture

INTRODUCTION

Groundwater resources are under increasing pressure in most parts of the world as a result of their exploitation in rural, residential and industrial areas [WAGH *et al.* 2016], a phenomenon that is amplified by the aridisation of certain areas under the influence of climate change [JACKSON *et al.* 2001]. As such, this resource is a key factor in the sustainable economic development of a region and its inhabitants [LI *et al.* 2017; SARAVANAN *et al.* 2016; ZHOU *et al.* 2016]. Knowledge of water chemistry can help to better understand the natural processes or human activities likely to have an impact on its composition [LIU *et al.* 2015; SELVAKUMAR *et al.* 2017]. Within an aquifer, this is generally through interactions with lithology and rock weathering, neoformations and precipitation, and ion exchanges [Ma *et al.* 2017]. The aridity of the climate also has a strong influence, concentrating the water, inducing a wide range of minerality very often leading to the salinisation of surface waters but also of aquifers. The mineralisation of waters leads to the formation of brines in the saline depressions of the Chotts and Sebkhats. In this respect, North Africa in general and Algeria in particular is evolving from a Mediterranean type climate to a desert type towards the Sahara [Houha *et al.* 2008]. The majority of lithological formations release high levels of calcium and therefore induces an evolution towards the neutral saline pathway for which calcium is higher than alkalinity in terms of charge concentration. Beyond these general considerations, which have been the subject of numerous studies on North Africa [Drias *et al.* 2020], there is the question of local variations in water quality, which can be influenced by numerous anthropic factors or by the spatial variability of the lithology of the catchment basins. Faced with a fairly scarce water supply due to rainfall that is mainly of orographic origin, there is a lack of knowledge on the quality of groundwater with a view to its preservation and sustainable exploitation.

The aim of this work is to characterise the chemistry of groundwater and determine the origin of the chemical elements present in the waters of the Foum El Gueiss basin in Algeria. The method is based on a multifactorial approach by Principal Component Analysis (PCA). In a second step we propose to measure the possible differentiation of water quality according to its origin (spring, well or borehole).

MATERIALS AND METHODS

THE STUDY AREA

The Foum El Gueiss sub-basin, with a surface area of 9615 km^2, is located on the high plateaus of Constantine at the northeastern part of Algeria. It is crossed by the Oued Gueiss, coming from the wooded northern slope of the Djebel Aourès before supplying the Chott El Mellah, annex of the endorheic basin of Garaat Al Tarf [Lessard 1952]. The predominant formations are Cretaceous, represented by the Aptian, the Albian and the Barremian [Lafitte 1939]. Quaternary terrains are also widespread, in the form of blocky slopes of the reliefs, and alluvium in the low and terraced areas (Fig. 1). Overall, in the basin, the soils are of medium to high permeability.

In the region, rainfall and other climatic parameters are influenced by the altitude and orientation of the mountain ranges [Cote 1974]. According to the calculations made on the climatic data of the meteorological station of El-Hamma for the period 1987–2015 [ONM 2018]; the climate is semi-arid with a cool winter, and relatively rainy with an average rainfall of about 423 mm and average potential and actual evapotranspiration of 426 mm and 213 mm, respectively, i.e. about 100% and 50% of precipitation. Actual infiltration, i.e. the proportion of water passing through the soil and supplying the aquifers, is estimated at 70.81 mm, representing about 17% of the rainfall. The agricultural deficit is estimated at about 230 mm, i.e. 54% of rainfall, and is spread over the months of December–January and May. Riedel's analysis underlines the biogeochemical link between subsoil temperature and groundwater quality [Riedel 2019].

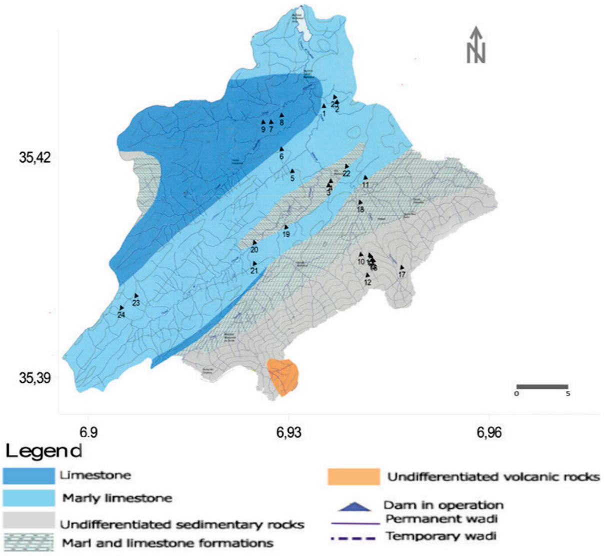

Fig. 1. Study area and waters sampling points; source: own elaboration

SAMPLING AND ANALYSIS TECHNIQUES

The distribution of the 25 groundwater sampling points is shown in Figure 1. The measurements of the physico-chemical parameters (pH, temperature and electrical conductivity) were carried out in the field using a multi-parameter device Consort c535. The samples were stored in polyethylene bottles in a cool, dark place [Rejsek 2002] and transported to the laboratory for analysis of the major ions by atomic absorption spectrometry [Rodier *et al.* 2009].

STATISTICAL TREATMENT

A principal component analysis was carried out using the correlation matrix to identify the sources of variability in the groundwater chemical profile of the catchment area. The original purpose of Principal Components Analysis (PCA) was to reduce a large number of variables to a much smaller number of principal components whilst retaining as much as possible of the variation in the original variables [Bencer *et al.* 2016; Jolliffe 2002].

For this calculation, as the temperature parameter is very fleeting, it was not taken into account. However, we have verified that this does not significantly alter the results. This was followed by a discriminant analysis to identify the main functions that distinguish between spring, well and borehole water. The calculations were performed using XLStat software (addinsoft), and the presentation is based on Piper and Wilcox diagrams drawn using Diagrams 5.6 and Globalmapper 13.

RESULTS AND DISCUSSION

CLASSIFICATION OF THE WATER

The Piper diagram is the most convenient method of plotting the results of several analyses on the same graph, which can reveal the clustering of certain samples and show different hydrochemical faces or origins of groundwater. It is made up of two triangles that represent the cationic and anionic facies, as well as a triangle that represents the global facies [MONITION 1966; PIPER 1953; THILAGAVATHI *et al.* 2012].

The chemical profile of the groundwater collected from the Foum El Gueiss basin is shown in the Piper diagram (Fig. 2). Two families of waters are observed, on the one hand, calcium and magnesian chlorated-sulphate waters, which account for 80% of the water points, and on the other hand, calcium and magnesian bicarbonate waters, which account for the remaining 20%. Calcium is the dominant cation, a general phenomenon in moderately concentrated waters as mentioned in the introduction. The calcium ions evolve in a range of 47 to 140 mg·dm^{-3}. These two families of water may reflect the effect of lithological heterogeneity or anthropic alteration.

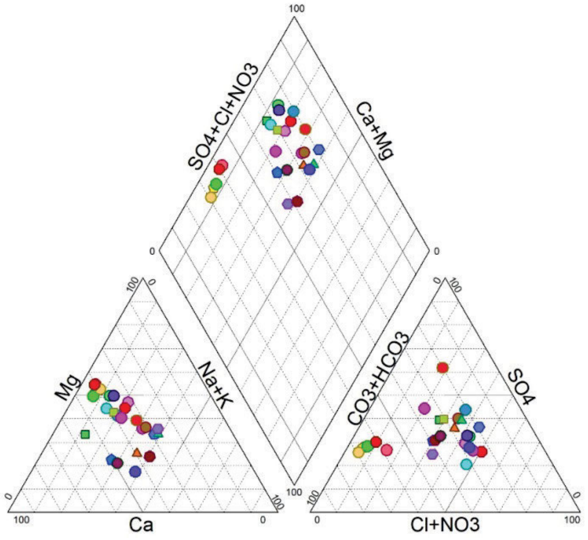

Fig. 2. Piper diagram for groundwaters of Foum el Gueiss watershed; source: own study

CHARACTERISTICS OF THE RELATIONSHIPS BETWEEN THE ELEMENTS

Relationship between Cl$^-$ and Na^{2+}: the solubility of chloride (Cl$^-$) in water is high and this ion interacts very little with the environment both in terms of saline precipitation (except for very high concentrations), as well as in terms of the phenomenon of ionic exchange or absorption by plants and micro-organisms. It is therefore frequently used to estimate a relative water concentration factor. In the most arid or endorheic environments, the solubilisation of halite can release chloride ions, but without affecting the relationship between Na^{2+} and Cl$^-$. Figure 3 shows scattered points and a rather poor correlation between these two ions, indicating distinct origins, including the absence of halite dissolution [GARCÍA *et al.* 2001; MOSAAD *et al.* 2019].

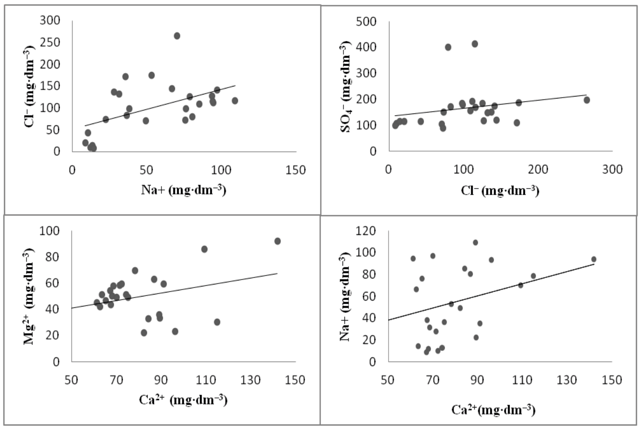

Fig. 3. Relationship between Na$^+$, Ca^{2+}, Mg^{2+}, Cl$^-$ and SO$_4^{2-}$ in groundwaters; source: own study

Relationship between Cl$^-$ and SO$_4^{2-}$: There is a closer correlation between these anions than for the Na^{2+}–Cl$^-$ ion pair. Two samples, however, departed markedly from the scatter plot, having much higher SO$_4^{2-}$ contents. It should also be noted that the correlation between Cl$^-$ and SO$_4^{2-}$ does not have a slope of 1, the increase in chloride contents being faster than that of SO$_4^{2-}$. This can be attributed to agricultural amendments, a pollution likely to increase the Cl$^-$ contents.

PRINCIPAL COMPONENT ANALYSIS (PCA)

The correlation matrix is presented in Table 1. The electrical conductivity (μS·cm^{-1}) shows a positive correlation with calcium (r = 0.82), secondarily with sulphates (r = 0.57), indicating that these ions are responsible for a significant part of the ionic charge.

Table 1. Preliminary findings of physicochemical parameters

Variable	pH	Salinity	*TDS*	*EC*	Ca^{2+}	Mg^{2+}	Na^{2+}	K$^+$	Cl$^-$	SO$_4^{2-}$	HCO$_3^-$	NO$_3^-$
pH	1.00											
Salinity	−0.01	1.000										
TDS	−0.22	**0.840**	1.000									
EC	−0.33	0.287	0.455	1.000								
Ca^{2+}	−0.27	0.226	0.305	**0.780**	1.000							
Mg^{2+}	−0.22	0.423	**0.505**	**0.522**	0.334	1.000						
Na$^+$	−0.01	−0.040	0.070	0.180	0.350	−0.110	1.000					
K$^+$	0.12	0.447	0.490	0.058	0.098	0.143	**0.624**	1.000				
Cl$^-$	0.04	0.485	**0.600**	0.372	0.389	0.315	**0.502**	**0.594**	1.00			
SO$_4^{2-}$	−0.18	0.136	0.268	0.425	**0.587**	**0.535**	0.458	0.305	0.225	1.000		
HCO$_3^-$	−0.35	−0.060	−0.060	0.486	0.367	0.434	−0.270	−0.310	−0.380	0.119	1.000	
NO$_3^-$	0.10	0.351	0.402	0.280	0.250	0.480	**0.500**	0.470	**0.630**	0.340	−0.02	1.00

Source: own study.

There is a correlation between sulphates on the one hand and calcium (r = 0.59) and magnesium (r = 0.54) on the other. Sodium correlates with potassium (r = 0.62), chlorides (r = 0.50) and nitrates (r = 0.50).

The first factorial plan alone accounts for more than half of the information (58%) contained in the dataset (Fig. 4). The first factorial axis (37%) is positively correlated to Ca^{2+}, Mg^{2+}, SO_4^{2-}, NO_3^- and K^+; this axis acontrasts low mineralised waters with calcium carbonate chemical profile and waters with chlorinated-sulphate profile and higher mineral load. This is an axis of concentration, which can be explained by the aridity of the climate; in arid and semi-arid areas, increased evapotranspiration can lead to salinisation of groundwater. The second factorial axis (21%) opposes the Ca^{2+}–Mg^{2+}–SO_4^{2-} chemical profiles to the Na^{2+}–Cl^- profile marked by the presence of nitrate, and therefore impacted by agricultural contamination. The third factorial axis (13%) is clearly weaker than the previous two. It is also opposing chemical profiles, nitrates not appearing in this case, therefore possibly linked to a lithological heterogeneity.

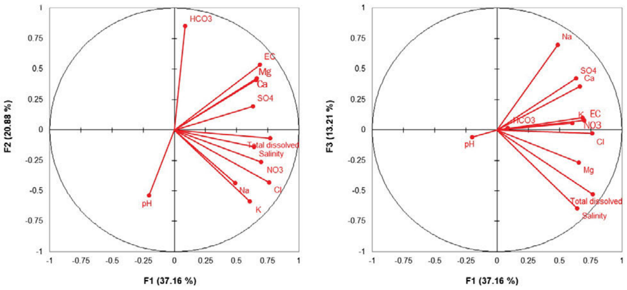

Fig. 4. Factorial plan of the Principal Component Analysis (PCA): a) F1–F2, b) F1–F3; source: own study

To summarise, the PCA shows that the main factor influencing the composition of major ions in the waters of this watershed is the increase in minerality from upstream to downstream of the basin under the influence of climate, which is usual in North Africa. The second most important process is the nitrogen contamination of the water resource, which highlight the impact of agricultural activity on the quality of groundwater in this region.

DISCRIMINANT ANALYSIS (DA)

As with the PCA, the DA presented here was conducted without integrating temperature, but considering this parameter does not change the results that follow. The first discriminant function is essentially marked by the high negative correlation of Cl^- and SO_4^{2-} (Tab. 2). The second discriminant function opposes the parameters Cl^-, SO_4^{2-} and NO_3^- to Ca^{2+} and Mg^{2+}. HCO^{3-} is highly positively correlated with the second discriminant which are probably the original natural.

The F1 function that marks the minerality mainly opposes springs to wells and boreholes, i.e. mountain water located upstream to groundwater located further downstream. However, the ellipsoids show a certain degree of overlap (Fig. 5a, b). The second function F2 opposes wells to springs and boreholes. This result suggests that the presence of nitrate appears to be marked in the vicinity of the wells.

Table 2. Standardised canonical discriminant function coefficients

Parameter	F1	F2
pH	0.461	0.341
Salinity	–0.009	0.537
Total dissolved load	–0.020	–0.281
EC	0.585	0.308
Ca^{2+}	–0.248	–1.981
Mg^{2+}	–0.036	–1.763
Na^+	–0.234	–0.051
K^+	0.674	–0.004
Cl^-	–0.959	1.362
SO_4^{2-}	–0.794	0.948
HCO_3^-	0.633	1.534
NO_3^-	0.091	0.577

Source: own study.

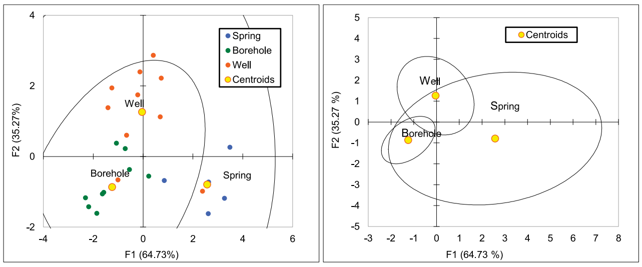

Fig. 5. Spring, well and borehole: a) centroid plots b) ellipse plots; source: own study

The confusion matrix (Tab. 3) on the dataset shows full discrimination (100% success rate), which attests to a real difference in composition between these three types of samples (wells, boreholes and springs).

Table 3. Confusion matrix for the estimation sample (100% success rate)

Specification	Spring	Borehole	Well	Total
Spring	5	0	0	5
Borehole	0	10	0	10
Well	0	0	10	10
Total	5	10	10	25

Source: own study.

However, in the confusion matrix for the cross-validation results (Tab. 4), there is some confusion between wells and boreholes, mainly due to their small degree of difference according to the second discriminating function, i.e. that which includes the presence of nitrate.

In summary, there is a real difference between spring water and other samples, while the difference between wells and

Table 4. Confusion matrix for the cross-validation results

Specification	Spring	Borehole	Well	Total	% correct
Spring	2	2	1	5	40.00
Borehole	0	3	7	10	30.00
Well	0	5	5	10	50.00
Total	2	10	13	25	40.00

Source: own study.

boreholes is smaller. The main confusion is between wells and boreholes, which is understandable because they are adjacent groundwater, rather in the lower part of the catchment area.

CONCLUSIONS

On the Foum El Guiess catchment area, two water families have been identified from the Piper diagram. They are characterised on the one hand by a $Ca^{2+}/Mg^{2+}–Cl^{-}/SO_4^{2-}$ chemical profile and on the other hand by the $Ca^{2+}/Mg^{2+}–HCO_3^{-}$ profile. The variability in the composition of the waters must be attributed primarily to the influence of the climate, which increases the minerality of the waters from upstream to downstream, but also to agricultural pollution in the lower areas. Two discriminating functions make it possible to distinguish samples according to their origin, i.e. spring, well or borehole water. These results constitute a basis for monitoring and preserving the water resources of this watershed.

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