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Statistical and hydrogeochemical characteristics of the M'Daourouch-Drea Plain's groundwater, North-East of Algeria

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Abstract

This work was conducted on 23 samples distributed between springs, wells and boreholes tapping the shallow and deep aquifer in the M'Daourouch-Drea area located in extreme northeast of Algeria. Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- and NO_3^- were analysed. The interpretation of the geological-geophysical data allowed us to highlight two aquifers. The first consists of conglomerates, sandstones, gravels, sands, marls, limestones, lacustrine and alluvial deposits varying in thickness from a few tens to a few hundred meters, representing Neogene-Quaternary filling of the studied basin. The second is more important localized in the cracked and karstified limestones of upper Cretaceous age; these limestones are outcropped on the flanks of the syncline and the borders of the basin. The first aquifer sometimes rests directly on the second which allows hydraulic communication between them. The hydrogeochemical and statistical study, with the combination of numerous tools, indicates that the chemistry of groundwater in the M'Daourouch-Drea Plain is controlled both by the dissolution of the minerals of the evaporite formations and those of the carbonate formations.

Key words: *groundwater, hydrochemical characteristics, M'Daourouch-Drea's plain, statistical characteristics*

INTRODUCTION

The M'Daourouch-Drea region is part of the high plains of northeastern Algeria and constitutes the Montesquieu syncline in the southwest of the Souk-Ahras district which covers an area of 96 km² (Fig. 1). The region's water needs have never ceased to increase and to meet the needs of a population exceeding 40,000 inhabitants; this resource is threatened with degradation after the establishment of some industrial units in the region and development importance of agriculture. A situation requires better knowledge of potential aquifers in the area. It is located 50 km South of the Souk Ahras province and far from the coast. The climate of the study area is con-

sidered to semi-arid climate, the annual average precipitation being approximately 465 mm. Rainfall occurs from august to June, with a maximum during January and February of each year. The average temperature is approximately 14.3°C in winter and 26°C in summer, though summer high temperature can reach 45°C in July. The mean annual potential evapotranspiration, according to the C.W. Thornthwaite formula, is approximately 875 mm. In addition to the tourist vocation, M'Daourouch-Drea belongs to the southern zone of the province with strong dominant sheep farming and cereal production. The main objectives of this study are to determine the main factors controlling the chemistry of these waters of M'Daourouch-Drea Plain's groundwater.

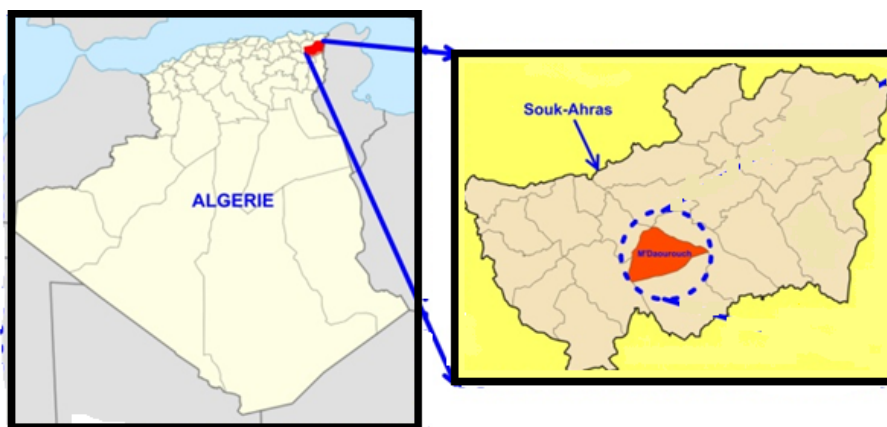


Fig. 1. Location of M'Daourouch-Drea Plain in Algeria; source: own elaboration

GEOLOGICAL AND HYDROGEOLOGICAL SETTINGS

The geology of the study area was investigated by several authors, i.e. CHOUABBI [1987], VILA [1980]. We will meet from the bottom up from bottom to top.

The oldest known outcrops on a regional scale are attributed to the Triassic age; these lands are in the form of diapiric structures in the north (diapir Souk-Ahras) and in the North-West (diapir of Djebel Tifech). These formations are intensely deformed, crushed and present virtually no normal relations with the overlying formations. The wall of the Triassic series is not known at the level of the studied plain. These lands are characterized by heterogeneity in their composition. It consists of blocks of limestones, sandstones, dolomites, all cemented by a gray-gypsum-clay matrix containing small fragments of the same rocks.

- Marly formations with calcareous intercalations, with a power exceeding 250 m, from upper Santonian to lower Campanian.
- Marly intercalated limestones (80–100 m) surmounted by limestone marls (50–70 m) of upper Campanian age.
- Limestones with rare marls intercalations (200–250 m) of lower Maastrichtian age surmounted by clayey marls and marly limestones (100–140 m) of upper Maastrichtian age.
- The Palaeogene is essentially marly (80–200 m). The whole is covered by recent Mio-Plio-Quaternary formations of conglomerates, sandstones, gravels, sands, marls, lacustrine limestones and alluvial deposits of varying thickness that can reach several hundred meters. This powerful predominantly terrigenous series participates in the filling of the intra-mountainous depressions and constitutes the hearts of the synclinal structures and becomes a potential aquifer reservoir.

From a tectonic point of view, the region is intersected by a fault network, which can be grouped into two main families, the first of orientation NW-SE and the second NE-SW and a series of parallel folds of main direction identical to second family of faults.

These two fault families often intersect and facilitate the infiltration of much of the runoff.

The plain is a Neogene filling characterized by its heterogeneity, consisting of conglomerates, sandstones, gravels, sands, marls, lacustrine limestones and alluvial deposits. This productive level rests directly on Cretaceous limestones, which probably permits an exchange of water between these two levels.

For a better recognition of the underground flows of the Neogene-Quaternary filling waters of the M'Daourouch-Drea Plain, a piezometric measure was carried out in May 2016, the results of which were used to develop the piezometric map (Fig. 2). The arrangement of the hydro-isohyps curves shows:

- two feeding areas from the lower Maastrichtian limestones forming the northwest and south-eastern borders of the study area;
- a groundwater convergence zone is located to the North-East of the plain where it is drained slightly South of the village of Drea to feed the main river in the region Laghedir Wadi;
- curve spacing is relatively stable indicating a stable hydraulic gradient over the studied area;
- the flow of groundwater follows the flow of Laghedir Wadi towards the downstream part of the plain, which makes it possible to demonstrate a feeding of this watercourse by the underground waters of the plain.

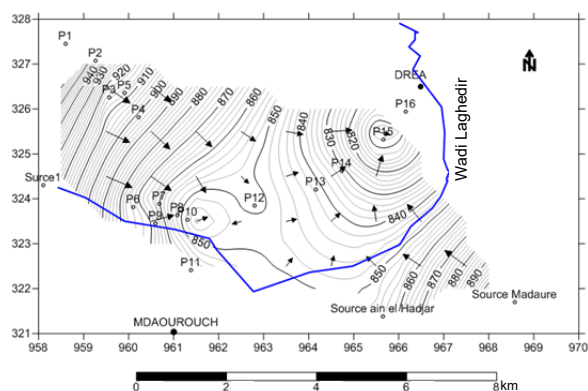


Fig. 2. Sampling points situation and head piezometric map of the waters of the M'Daourouch-Drea Plain's; May 2016; source: own study

GEOPHYSICAL CONTEXT

The correlation between the results of the vertical electrical soundings established during the electrical prospection studies [ALGEO 1982; ICOSIUM 2001] with the logs of the mechanical soundings enabled us to establish some values of resistivities of the geological formations of the M'Daourouch-Drea region for a lithology-resistivity correspondence (Tab. 1). This

Table 1. Resistivity value of the main formations of the M'Daourouch-Drea region

Lithology	Age	Resistivity, $\Omega\cdot m$
Limestone crust	Quaternary	170–610
Clays, marls and sands	Mio-Pliocene	2–30
Sand and sandstone	Mio-Pliocene	30–70
Sandstone and conglomerates	Mio-Pliocene	80–140
Whitish limestones	Maastrichtian	40–180

Source: own study.

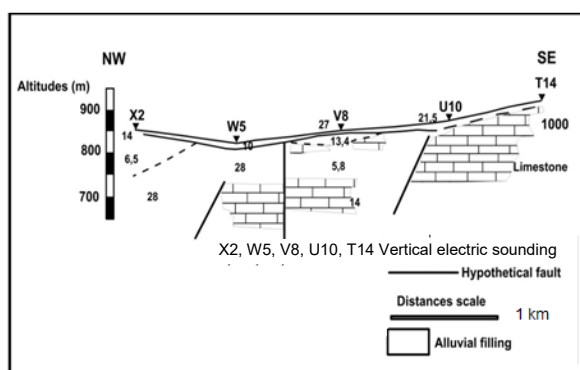


Fig. 3. Cross-section and vertical electric sounding position in the study area; source: own elaboration

information is useful for locating the depth of the Maastrichtian limestones and consequently the geometry of the undergrowth of the Neogene-Quaternary filling.

The geo-electric cross section (Fig. 3), made to the North of the village of M'Daourouch with orientation NW-SE, shows compact resistant limestones on the edge of the plain, then become faulted and deepen in the form of stairs with low resistivities in the middle of the plain. The whole is covered by a formation with variable resistivity of very low to average characteristic of alluvial formations.

MATERIALS AND METHODS

Sampling and analytical methods groundwater samples were collected for geochemical analysis at different depths from 23 production wells tapping the shallow aquifers during May 2016 (Fig. 2). Electrical conductivity and pH were measured *in situ* using a multiparameter WTW set (Multiline P3 PH/LF SET). At the same

time, samples of nonacidified water were taken in 1.5 dm³ polyethylene bottles and stored in darkness at 4°C. Chemical analyses were undertaken at the laboratory of the Department of Geology at the University of Constantine. The bicarbonates and carbonates were measured immediately after sampling by titration with the methyl orange endpoint; the concentration of chloride was determined by titration and precipitation of AgCl until silver chromate appears (Mohr's method); sulphate was determined by the nephelometric method; and nitrate, were analysed by the colorimetric method. Calcium and magnesium were determined by complex metric titration, and emission spectrometry was used to determine the concentration of sodium and potassium [RODIER 1996].

The identification of water facies was carried out by the software «Diagrams» [SIMLER 2014] by projecting the points directly on the diagram of piper. A statistical analysis of the data was performed starting with a descriptive statistic of the measured parameters, ending with a multiple correlation by a principal component analysis (PCA).

RESULTS AND DISCUSSIONS

IDENTIFICATION OF CHEMICAL FACIES IN WATER

The projection of the results of the chemical analyses on the Piper diagram (Fig. 4) shows that the points analysed in the region are grouped into two chemical families: bicarbonate and chloride. The analysis of the results indicates that in 70% of the cases the waters are bicarbonated whereas chlorinated waters are present in 30% of the cases (Tab. 2). Calcium accompanies bicarbonates and chlorides except

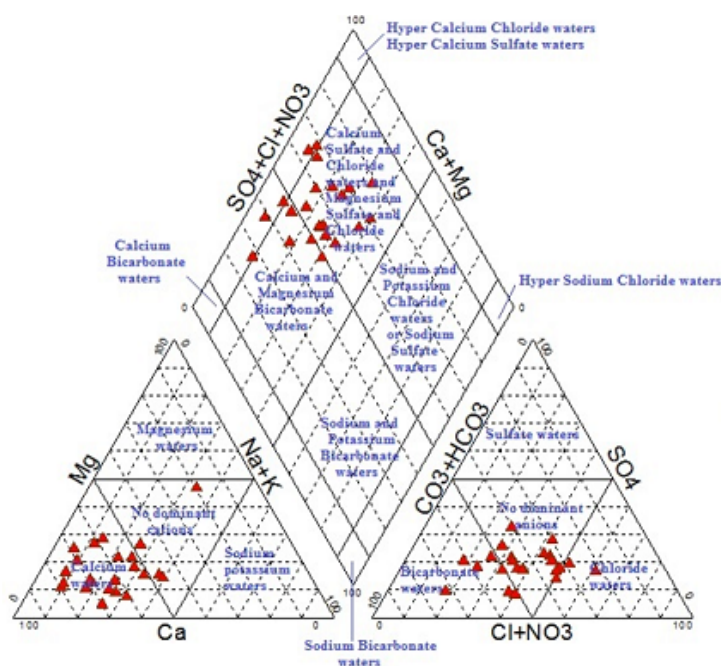


Fig. 4. Projection of the results on the Piper diagram; source: own elaboration

Table 2. Characteristics of the chemical facies of the analysed waters

Chemical facies		Characteristic formulas	Percent	Observation
Bicarbonate water	bicarbonate calcium	$r\text{HCO}_3^- > r\text{Cl}^- > r\text{SO}_4^{2-}$	69.57	SO ₄ is in 2 nd place in some cases
		$r\text{Ca}^{2+} > r\text{Na}^+ > r\text{Mg}^{2+} > r\text{K}^+$		Mg is placed in 2 nd position in some cases
Chlorides	chloride calcium	$r\text{Cl}^- > r\text{SO}_4^{2-} > r\text{HCO}_3^-$	26.09	-----
		$r\text{Ca}^{2+} > r\text{Mg}^{2+} > r\text{Na}^+ > r\text{K}^+$		-----
	magnesium chloride	$r\text{Cl}^- > r\text{HCO}_3^- > r\text{SO}_4^{2-}$	4.35	-----
		$r\text{Mg}^{2+} > r\text{Na}^+ > r\text{Ca}^{2+} > r\text{K}^+$		-----

Source: own study.

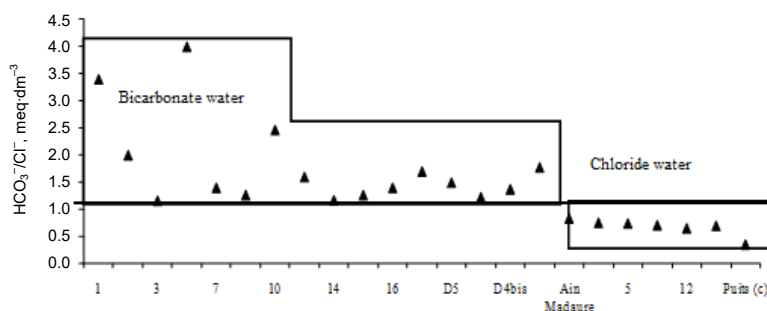


Fig. 5. Representation of the $\text{HCO}_3^-/\text{Cl}^-$ ($\text{meq}\cdot\text{dm}^{-3}$); 1–16, D5, D4bis, C = wells, Ain Madaure = spring; source: own study

for a single sample where magnesium dominates. The ratio $\text{HCO}_3^-/\text{Cl}^-$ indicates mixed water, the passage from one facies to another is however possible, it is noted that only 4 samples have a ratio greater than 2 (Fig. 5).

Let us recall the existence of a Triassic diapir that flushes to the North-West of the study area (Djebel Tifech and the diapir of Souk-Ahras), knowing that the Trias can arrive in sub-surface through numerous accidents that affect the region, on the one hand, and the Neogene filling of the studied syncline constituted by conglomerates, sandstones, gravels, sands, marls, lacustrine limestones and alluvial deposits on the other. We would expect a dominant facies of evaporite type generated by these formations. We find that the minerals of the carbonate rocks control the chemistry of the studied waters, so we think that this can be explained by two hypotheses:

- the majority of the water points analysed capture the limestones especially at the periphery.
- the two layers (filling and Cretaceous) are in direct contact allowing a water exchange; in reality, both hypotheses are involved in the development of the chemistry of the studied waters; indeed, the boreholes, particularly from the edge of the plain, capture the limestones and the two levels (filling and Cretaceous) are in direct contact, without a waterproof screen, so we can expect a mixture of the waters of the two levels.

STATISTICAL ANALYSIS

Elementary statistics and correlation matrix.

The descriptive statistics of the physicochemical and chemical parameters analysed for the periods (8 normalized variables: Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} ,

HCO_3^- , NO_3^-) of this study are summarized in Table 3. Dominate cations are sodium and calcium, which have an average concentration of 124.78 ± 46.74 and 56.77 ± 37.56 $\text{mg}\cdot\text{dm}^{-3}$, respectively. Bicarbonates are generally the major anion, having an average concentration of 259.66 ± 85.56 $\text{mg}\cdot\text{dm}^{-3}$, followed by Cl^- (average concentration, 145.93 ± 21 $\text{mg}\cdot\text{dm}^{-3}$) and SO_4^{2-} with an average of 93.36 ± 47.87 $\text{mg}\cdot\text{dm}^{-3}$.

To illustrate anomaly between physico-chemical parameters; it is assumed that a CV less than 50% demonstrates certain homogeneity in the amplitude of the observed values between minimum and maximum values reflecting a small variation around the average. On the other hand, parameters with a CV greater than 50% indicate a large deviation from the average of all the observations and therefore the variation of the concentrations in a wide range (Tab. 3).

This parameter is high for some elements such as potassium (150%), magnesium (83%), sodium (66%), and to a lesser extent chlorides (51%). On the other hand, the ions of the carbonate minerals (Ca^{2+} and HCO_3^-) show a fairly regular variation in the aquifer ($\text{CV}\% = 30\%$). This can be attributed in our case to the influence of rapid dissolution of evaporate minerals giving high grades in contrary of carbonated minerals.

The contribution of the correlation between the physicochemical parameters in the groundwater helps to understand some phenomena released by the water-rock interaction. It gives an approach on the common origin of certain parameters. It is assumed that a correlation is significant if the value of the correlation coefficient r is between +0.537 and 1 (positive relationship) and -0.5 and -1 (negative relationship). In our case, several links are significant and can be attributed to geological causes, but to varying degrees (Tab. 4).

Table 3. Descriptive statistics of the physicochemical data

Parameter	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	EC	pH
	mg·dm ⁻³									
Average	124.78	23.43	56.77	1.83	145.93	93.36	259.66	60.96	10 800	7.49
Minimum	64.13	4.80	11.96	0.05	35.50	25.00	158.60	13.00	584	7.20
Maximum	256.00	92.36	134.00	12.00	319.50	215.00	506.00	120.00	1 936	7.80
SD	46.74	19.40	37.56	2.75	74.21	47.84	85.56	20.21	355.40	0.18
CV%	37.46	82.81	66.17	150.06	50.85	51.24	32.95	33.15	32.91	7.46

Explanations: EC = electrical conductivity, SD = standard deviation, CV% = coefficient of variation.

Source: own study.

Table 4. Matrix of the correlation coefficients of the physicochemical of water samples

Parameter	Ca ²⁺	Mg ²⁺	Na ⁺	K ⁺	Cl ⁻	SO ₄ ²⁻	HCO ₃ ⁻	NO ₃ ⁻	EC	pH
Ca ²⁺	1									
Mg ²⁺	0.065	1								
Na ⁺	0.537	0.598	1							
K ⁺	0.796	0.058	0.654	1						
Cl ⁻	0.602	0.770	0.826	0.510	1					
SO ₄ ²⁻	0.655	0.553	0.716	0.488	0.746	1				
HCO ₃ ⁻	0.827	0.103	0.675	0.810	0.545	0.601	1			
NO ₃ ⁻	-0.326	0.643	0.176	-0.471	0.351	0.047	-0.348	1		
EC	0.652	0.711	0.684	0.406	0.875	0.863	0.528	0.257	1	
pH	0.288	0.065	0.228	0.319	0.153	0.433	0.263	-0.279	0.339	1

Explanations: in bold, significant values $p = 0.05$.

Source: own study.

The correlation matrix shows that the electrical conductivity (EC) has a very high significant relation with, Mg²⁺, Cl⁻ and SO₄²⁻. This reflects the participation of these elements in the acquisition of water mineralization. This relationship is less important with bicarbonates. Calcium has a strong positive correlation with bicarbonates (0.827), sulphate (0.655) and chlorides (0.602), indicating both a carbonated and evaporitic origin of this ion (Tab. 4). Similarly for Na⁺-Cl⁻ (0.826), Na⁺-SO₄²⁻ (0.716) and SO₄²⁻-Cl⁻ (0.746) which also have a good positive correlation (Tab. 4). The high levels of Na⁺, Cl⁻, Ca²⁺ and SO₄²⁻ detected in some samples may suggest the dissolution of chloride and sulphate salts (Tab. 4).

We note also that the nitrates seem to have an anthropogenic origin; its connection with the conductivity (indicator of mineralization) is insignificant. This reflects the participation of these elements in the acquisition of water mineralization. We note also that the nitrates seem to have an anthropogenic origin; its connection with the conductivity (indicator of mineralization) is insignificant.

Principal component analysis. In order to evaluate the different processes that affect the evolution of hydrogeochemistry of the study area, principal component analysis (PCA) were applied. PCA is a method which includes reducing the overall number of variables to a smaller number, without losing essential information. It converts the data matrix into a new set of principal components based on the variance-covariance matrix. This statistical method has been widely applied for the study of water hydrochemistry throughout the world [ANAZAWA, OHMORI 2001; GÜLER, THYNE 2004; THIVYA 2013; YIDANA *et al.* 2008] and in Algeria [BELKHIRI *et al.* 2010; BRINIS *et al.* 2014; 2015; MAOUI *et al.* 2010; NOUAR, BRAHMIA

2016]. The loadings and contribution for each parameter are summarized in the Table 5. The results of the multivariate analysis indicate that 78.52% of cumulative variance is acceptable to explain the chemistry of the investigated groundwater (Fig. 6). Factorial axis 1 which explains 54% of the variance has high and positive loadings (>0.70) driven by EC, Ca²⁺, Na⁺, K⁺, HCO₃⁻, Cl⁻ and SO₄²⁻ suggest that this variable association is referring to the dissolution of geological rock of the Cretaceous and gypso-saliferous carbonate minerals of the Neogene-Quaternary and/or Triassic filling, Factorial axis 2 (24% of the variance) is represented positively by Mg²⁺ and NO₃⁻ suggest that this variable association is referring to the dissolution of geological rock components and pollution of water by artificial fertilizers. On the circle of variables, we notice the grouping of the ions in two distinct poles, the first evaporitic associated with the conductivity is clearly visible to the right of the axis F1, while the

Table 5. Loading and contribution (%) for the factor matrix of the two-factor model that explains 78.52 % of the total variance

Elements	Axis F1		Axis F2	
	loadings	contribution, %	loadings	contribution, %
Ca ²⁺	0.801	11.840	-0.434	7.755
Mg ²⁺	0.577	6.145	0.750	23.112
Na ⁺	0.873	14.066	0.136	0.766
K ⁺	0.733	9.914	-0.543	12.117
Cl ⁻	0.895	14.788	0.349	5.001
SO ₄ ²⁻	0.884	14.401	0.081	0.271
HCO ₃ ⁻	0.788	11.464	-0.449	8.297
NO ₃ ⁻	0.027	0.014	0.935	35.973
EC	0.889	14.575	0.282	3.276
pH	0.389	2.794	-0.289	3.432

Source: own study.

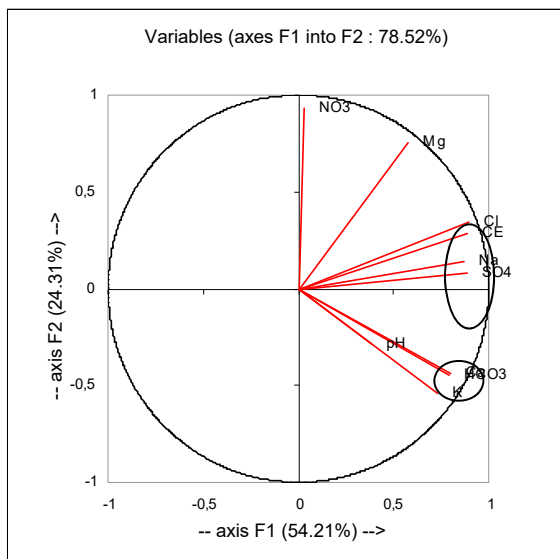


Fig. 6. Projection of variables; source: own study

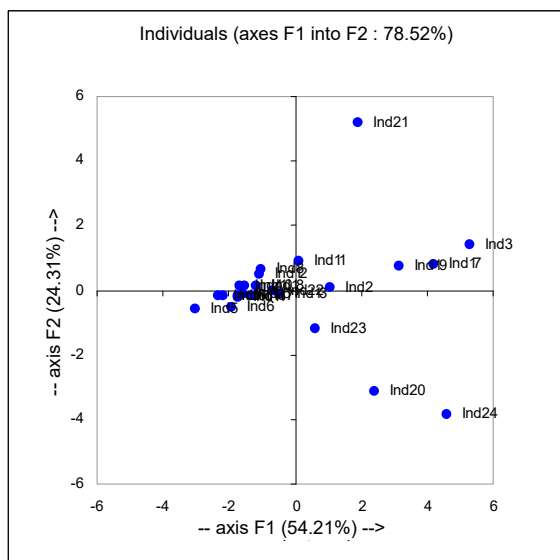


Fig. 7. Projection of individuals on factorial F1 / F2; source: own study

second is that of the mineralization due to the carbonates encompassing HCO_3^- and Ca^{2+} (Fig. 6). On the F1/F2 plane of the individuals, the majority of the samples cluster in the center of the circle indicating average mineralization, however, some points (3, 17, 19, D4bis and D3) indicate excessive mineralization whereas the well (c) shows significant pollution by nitrates ($120 \text{ mg}\cdot\text{dm}^{-3}$). Both factors show that the groundwater of the region is influenced by the dissolution of two types of minerals: evaporitic and carbonate, with the presence of nitrate pollution indices (Fig. 7).

The concentration factor established from the chloride data dissolved in the groundwater indicates the evolution of the overall mineralization. The diagrams (Fig. 5) show that all elements do not evolve in proportion to the concentration factor. Thus one notices several trends:

- elements that perfectly follow the evolution of the concentration factor and concentrate in identical ways are the elements generated by the evaporate minerals.
- dice that evolve independently of the overall concentration (concentration factor) and seem to focus in different ways.

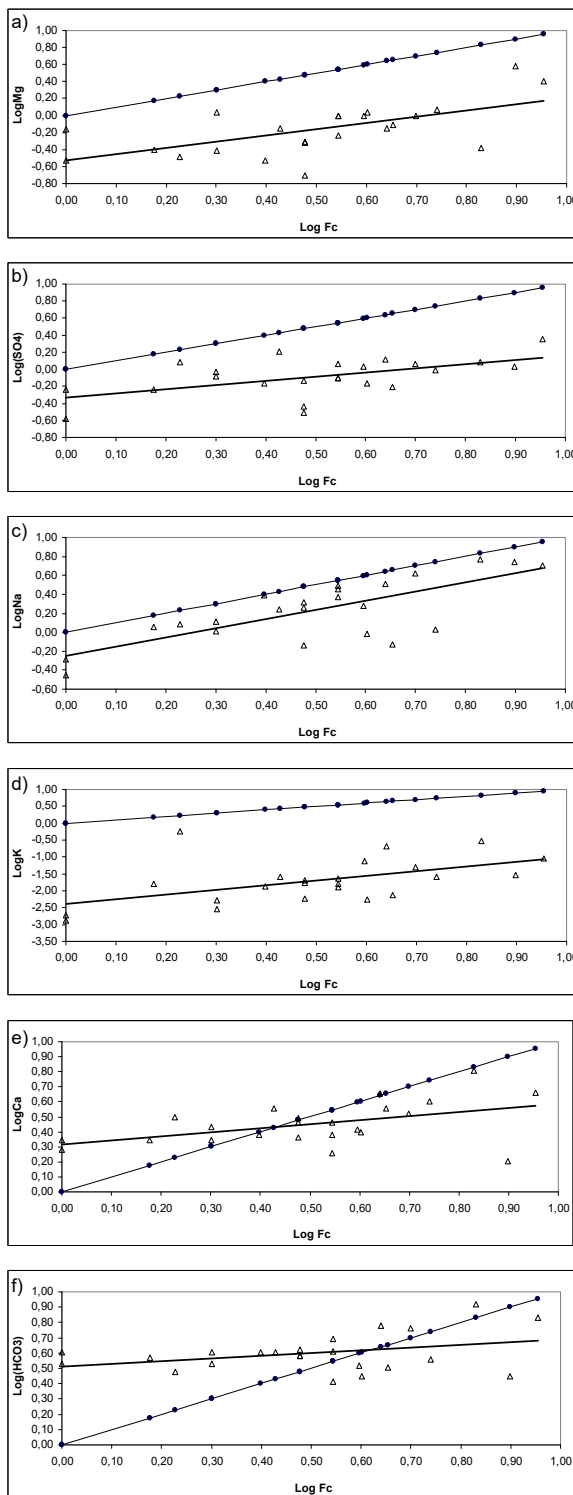


Fig. 8. Concentration diagram of: a) LogMg^{2+} b) LogSO_4^{2-} , c) LogNa^+ , d) LogK^+ , e) LogCa^{2+} , f) LogHCO_3^- ; source: own study

Evolution of evaporate ions. The diagrams presented in Fig. 8 show a perfect evolution of the evaporate elements with the concentration factor (CF). This indicates a common origin which is related to the dissolution of Neogene-Quaternary filling formations or probably the influence of Triassic intrusions which appear in diapir on the side of Djebel Tifech and Souk-Ahras. The enrichment of the water in ions of these minerals is done gradually according to the CF . We believe, therefore, that if the waters of the carbonate formations had not disturbed the chemistry of the aquifer of the filling, it would then be characterized by an evaporate facies of the saliferous or gypsumiferous type. Knowing that 70% of the water analysed is of bicarbonate facies, this is an argument of the dominance of carbonates in a mixture of the waters of the two chemical families (evaporated and carbonated).

Evolution of carbonate. The dissolution of limestones (calcite) generates calcium and bicarbonates, these two elements are in close connection (correlation coefficient = +0.827) therefore a same origin. The Figures 8e and 8f showed an evolution which does not follow that of the concentration factor (CF). The waters are already saturated with calcium and bicarbonates at the beginning of the enrichment of the waters in mineral salts. The slope of the lines of calcium and bicarbonates is lower than that of the concentration factor.

Moreover, we note that magnesium does not have a role with this group, the mode of its evolution attribute to it an evaporate origin.

Taking into account the HCO_3^-/Cl^- ratio, we believe that the chemistry of the waters would be the product of the dominance of the waters of the Cretaceous carbonate formations in a mixture with the waters of the Neogene-Quaternary filling formations. The water points where the ratio HCO_3^-/Cl^- is important, the waters would be captured directly in the limestones without mixing.

CONCLUSIONS

The plain of M'Daourouch-Drea is limited by tectonic accidents, the corresponding basin is the result of a Neogene-Quaternary filling up of heterogeneous formations (conglomerates, sandstone, gravel, sand, marl, limestone and lake sediments), resting directly on a calcareous substratum of Cretaceous age, the contact between these two levels is direct due to the lack of an impermeable level between them, which allows an exchange of water whence the mixing of the waters of the two layers. The feeding of the filling takes place from the reliefs in the North-West and the South-East. The flow converges to the North-East. The chemistry of the groundwater of this plain is controlled both by the dissolution of the minerals of the evaporate rocks and those of the carbonate rocks. The combination of statistical and hydrogeochemical analysis confirms the existence of these two families,

although they originate from two distinct aquifers (filling and cretaceous) that appear to be mixed. The HCO_3^-/Cl^- ratio close to 1 confirms this mixture (no net dominance of anion on the other). Monitoring the evolution of mineralization using the concentration factor (CF) indicates that ions of evaporate minerals evolve well with this factor, in contrast to ions of carbonate minerals that are already saturated with calcium and bicarbonates at the beginning of the concentration. The waters of the Cretaceous (carbonate) mix with the waters of the filling rich in evaporate ions and enrich themselves more in these latter. The results are mixed waters with a dominance of bicarbonate waters (70% of the samples).

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Statystyczna i hydrogeochemiczna charakterystyka wód podziemnych M'Daourouch-Drea, północny-wschód Algierii

STRESZCZENIE

W pracy przedstawiono wyniki badań, których podstawą były 23 próbki wód podziemnych pochodzących ze źródeł, studni kopanych i wierconych służących czerpaniu wody z płytkiego i głębokiego poziomu wodonośnego na obszarze M'Daourouch-Dréa w północno-wschodniej Algierii. W próbkach analizowano stężenie Ca^{2+} , Mg^{2+} , Na^+ , K^+ , Cl^- , SO_4^{2-} , HCO_3^- i NO_3^- . Interpretacja danych geologiczno-geofizycznych ujawniła istnienie dwóch poziomów wodonośnych. Pierwszy zbudowany jest z konglomeratów, piaskowców, żwirów, piasków, margli, wapieni i osadów aluwialnych o miąższości od kilkudziesięciu do kilkuset metrów, które reprezentują czwartorzędowe wypełnienie basenu. Drugi, ważniejszy, zlokalizowany jest w spękanych krasowych wapieniach górnej kredy. Wapienie te mają miejscami wychodnie na obrzeżach synkliny i przy granicach basenu. Pierwszy poziom wodonośny zalega w niektórych miejscach nad drugim, co umożliwia łączność hydrauliczną między obydwoma poziomami. Badania hydrogeochemiczne i statystyczne w połączeniu z różnymi narzędziami wskazują, że skład chemiczny wód gruntowych na terenie równiny M'Daourouch-Dréa zależy od rozpuszczania minerałów z formacji ewaporatowych oraz z utworów węglanowych.

Słowa kluczowe: *charakterystyka hydrochemiczna, charakterystyka statystyczna, równina M'Daourouch-Dréa, woda podziemna*