

Assessment of groundwater mineralization in the arid steppe region of the Messaad plateau aquifer, Southern Algeria

Serhane Brahmi^{1,✉}  0000-0001-6371-8018

Badreddine Rahmani²  0009-0005-2547-3263

Ali Nesrat²  0009-0009-6547-8666

Cehili Djamal²  0000-0003-3779-2235

Smail Brahmi²  0000-0002-8001-057X

¹ Mines and Geotechnology, Mining Institute, Echahid Cheikh Larbi Tebessi University, Algeria

² Sciences of Earth and Univers, Echahid Cheikh Larbi Tebessi University, Algeria

✉ Corresponding author: serhanebrahmi@univ-tebessa.dz

Summary

Water scarcity is severely high in the North Africa and the Middle East (MENA) regions. The deterioration of water quality has an impact on the human health as well as on the development of agricultural activities, especially in arid regions, where precipitations are less frequent. The aim of this work is to identify and evaluate the chemistry of the groundwater aquifer in the region of Messaad plateau. This region is located 370 km south of Algiers in southern Algeria. A dozen of samples were collected from wells and analyzed using physic-chemical technics, and the results were processed statistically. The distribution of the conductivity values and the various chemical parameters suggest that the groundwater in the Messad wadi area is overall highly mineralized, with the EC ranging from $550 \mu\text{S} \cdot \text{cm}^{-1}$ to $8790.13 \mu\text{S} \cdot \text{cm}^{-1}$, with a predominance of calcium sulphate facies and calcium chloride facies. The level of mineralization noted in the southern and southeastern portions of the research area sheds light on the source of natural contamination. The SO_4^{2-} , Cl^- , Ca^{2+} , Na^+ ions are the most important factors influencing the electrical conductivity of water and the groundwater chemistry. These ions are the result of the continuous dissolution of gypsum and halite in the clays and marls of the Barremian formations.

Keywords

Barremian aquifer • mineralization • groundwater origin • Messaad • Algeria

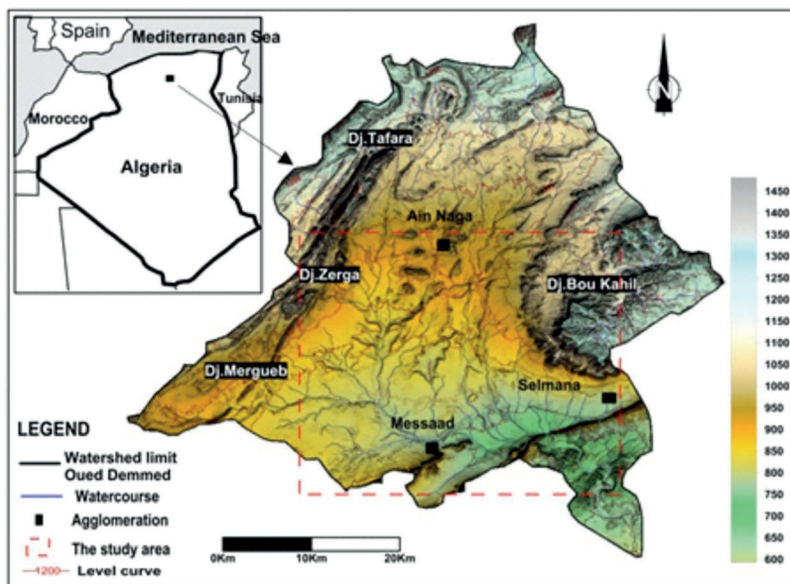
1. Introduction

The deterioration of water quality in North Africa and Middle East is a problem for human health as well as for the development of agricultural activities, especially in arid regions, where water resources are scarce [Brahmi et al. 2021, Brahmi et al. 2022, Missaoui et al. 2023]. The study area (Messaad plateau) lies in the arid zones of Algeria. It is located 370 km south of the Algiers, and it is known for its agricultural and agro-pastoral vocation. Currently, agriculture is booming and therefore requires large quantities of water resources [Nesrat et al. 2023] to meet the needs of the region with a view to achieving sustainable development. The never-ending issue of supplying water to the agriculture is the scarcity of water due to the rainfall irregularity. Under these conditions and with the decrease of surface water resources, the Barremian is the main aquifer in the region, and the most sought after by the population and the rural community of the steppe area. Large-diameter wells and boreholes are used to exploit the aquifer for irrigation and water supply to households in the vulnerable area, affecting the overall water resources. In addition, natural factors related to geological constraints have an effect on the quality of groundwater [Fehdi et al. 2011, Hamed 2016, Besser et al. 2017]. Pollution can also play a role in the degradation of water quality, because the domestic wastewater is being discharged directly into the Oued Messaad stream that crosses the city from west to east, this wastewater can infiltrate through the porous layers and pollute the shallow aquifer [Henri 1971, Brahmi et al. 2021]. The previous hydrogeological studies carried out in the area were insufficient as they did not discuss the groundwater quality [Hydrog 2000, Hidouche 2003]. However, the discussion of the results of some physical analyses of the shallow aquifer in a few wells provided by the ANRH (Agence Nationale des Ressources Hydriques) shows significant values of the chemical elements exceeding the standards set by the WHO (World Health Organization), with conductivity values exceeding $2000 \mu\text{S} \cdot \text{cm}^{-1}$. These values show a deterioration in groundwater quality, so it is essential to quantify and analyze the quality of the water supply and to understand how to manage this resource to ensure sustainability. The main issues of the present study include the examination of the hydrogeological and the geological factors controlling the physico-chemical characteristic of the groundwater quality and affecting the water salinity in the Barremian aquifer, and the description of groundwater chemistry.

2. Presentation of the study area

The Messaad Plateau is located 370 km south of Algiers and covers an area of 950 km². It is situated about 75 km south-east of Djelfa province, and 60 km north of the province of Laghouat, the Plateau is bounded by longitudes $3^{\circ}13'0.30''$ and $3^{\circ}39'8.33''$ and latitudes $34^{\circ}4'23.07''$ and $34^{\circ}20'31.56''$. The massifs of the Djebels: Mergueb, Zerga, Tafara and Boukahil (Fig. 1) create a natural boundary, and the altitudes vary from 600 to 1460 m a.s.l. The plateau covers mainly to the west of the large Chott Melghigh basin, more precisely, in the submerged part of the Oued Demmede sub-basin (code 06–06).

Since the Messaad Plateau belongs to the southern part of the Central Saharan Atlas, it has an arid continental climate, characterized by a cold winter with average annual precipitation of 150 mm, and average temperature of 19°C.



Source: Authors' own study

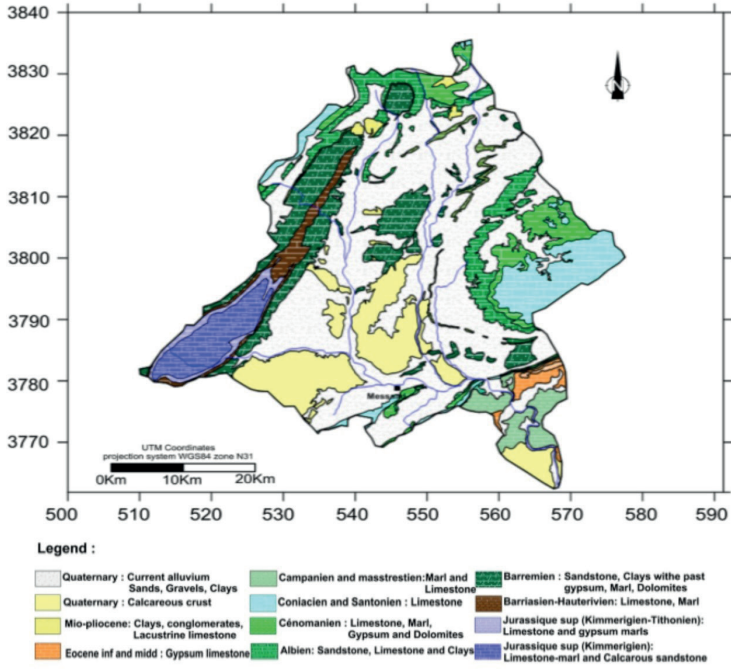
Fig. 1. Study area

3. Geological and hydrogeological settings

Oued Demmede basin is curved with facies of continental age, from Jurassic, Cretaceous, Tertiary and Quaternary [Basseto and Guillemot 1971, cited by Pouget 1977] (Fig. 2a).

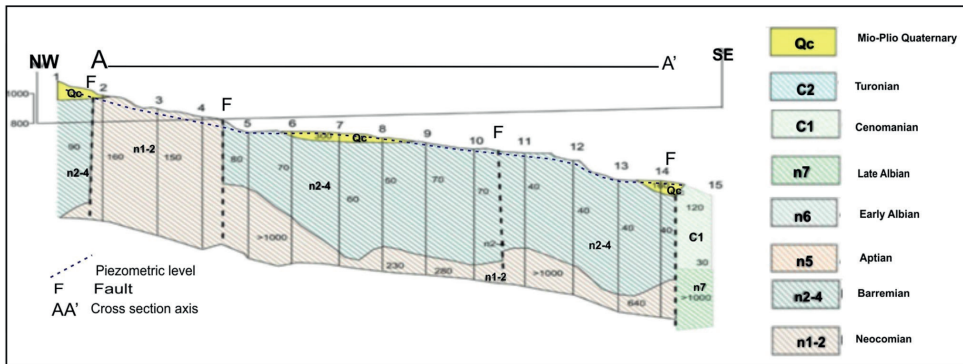
Non-tectonised, detrital superficial formations of the Mio-Plio-Quaternary (MPQ) form the porous aquifer. The Cretaceous formations are alternated series: mainly hard limestone, more or less dolomitic, with predominantly thin marl-limestone alternating with marl, and sandstone with intercalations of versicolored gypsum and saline clays. The Upper Jurassic (the core of the anticline of Dj. Zerga and Dj. Mergueb) is a metric alternation of limestone benches (beige limestone, lithographic microcrystallized grey and blue limestone, greyed limestone) and decametric strata of yellowish or green, blue and beige marls [Pouget 1977].

The tectonic inversion leads to a folding of the Messaad structure. Four faults cut the Barremian levels from NE to SW. There is a network of deep faults in the center of the plain (Fig. 2b), with a major fault connected to the boundary of Dj. Zerga [Beregh 2001]. However, the network does not affect the Mio-Plio-Quaternary levels. The erosion of the MPQ fine grain layer after the many and intense heavy rains has created



Source: Authors' own study

Fig. 2a. Schematic geological map of the Oued Demmede Basin



Source: Authors' own study

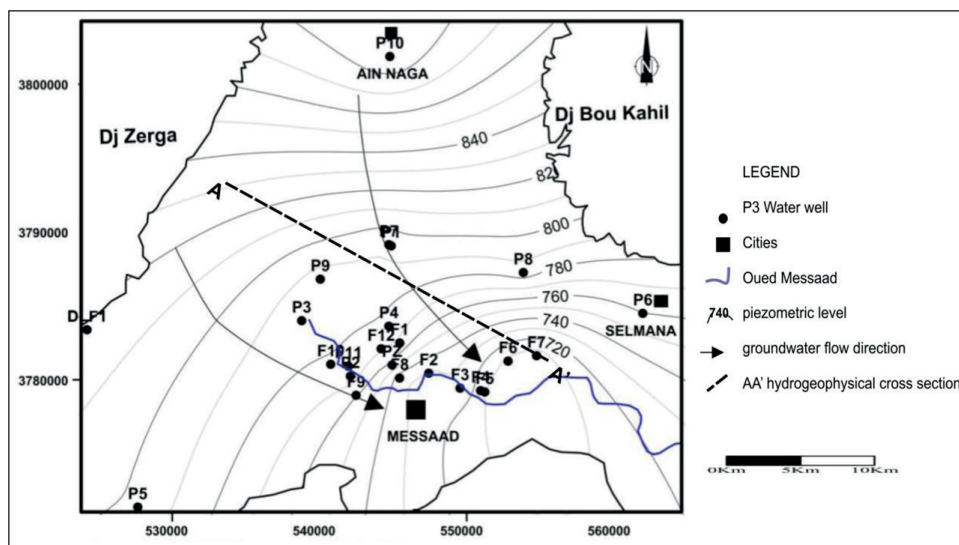
Fig. 2b. Geological and hydrogeological cross section adapted from geoelectrical data

a watershed, where the Mesaad Wadi contributes temporarily to the recharge of the shallow aquifer. This watershed runs along the direction of the underground aquifer, with a main underground flow direction NW-SE. The tectonic inversion developed over different layers indicates that the sandstone and limestone from Jurassic and

Cretaceous form – in hydrogeological terms – the most important aquifers [Hidouche 2003]. The study of the piezometric map reveals a recharge area along the borders of Dj. Tarafa in the north, Dj. Zerga and Dj. Mergueb in the west, and Dj. Bou Kahil in the east. The static level in the south-east part is over 4–15 m, and the depth of the water in the north-west part exceeds 30m.

4. Sampling and analysis

As part of this work, three campaigns of sampling water were conducted in November 2016, December 2017 (winter water table) and July 2018 (summer water table) (Fig. 3). A total of 31 samples were collected from groundwater wells and boreholes of Barremian and adjacent shallow MPQ aquifers. These samples were taken manually at the top of the borehole after a moment of flushing to remove the stagnant water in order to obtain representative samples of the groundwater. The samples are collected with bottles of 1000 cm³ capacity and kept in (4 degrees C) before chemical analysis. Three physico-chemical parameters (T°, pH, electrical conductivity) were measured in situ, immediately after sampling using a pHep pH meter (HANNA), and a Delta OHM HD 3406.2 field conductivity meter. The water analyses were carried out at the Water and Environment Laboratory of the Tébessa University. The volumetric method was adopted for the (Ca²⁺, Mg²⁺, Cl⁻, HCO₃⁻) elements. The (Na⁺, K⁺, SO₄²⁻) elements were approached using atomic absorption spectrophotometry by the Algerian Water Company (AWC) in 2016 and 2017. For the reliability of the analysis results, the ion balance method was applied and an error of 5% was accepted.



Source: Authors' own study

Fig. 3. Piezometric map of the Barremian (July 2018)

5. Results and discussions

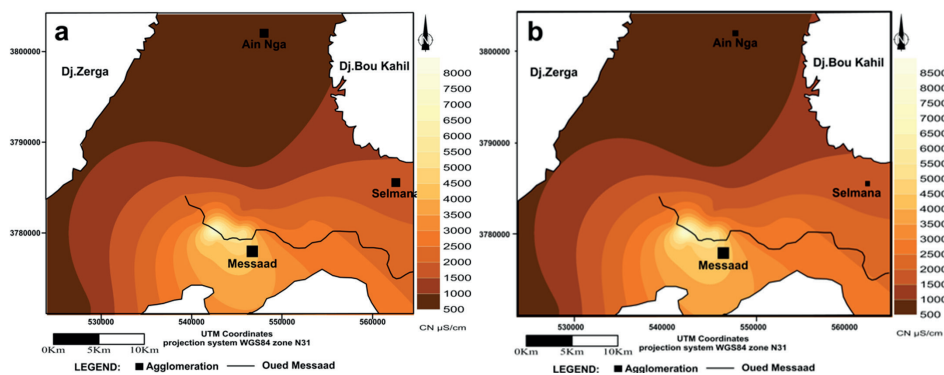
The groundwater physico-chemical analysis results are summarized in Table 1. The pH measurement of the sensitive area shows the value varies from well to well. The pH in the summer water table samples varies between 7.2 and 7.6, whereas in the winter water table samples it varies between 7.4 and 7.8. The temperature of the collected water ranges between 16 and 22.5°C. This variation in the temperature of the groundwater can be related to the depth of the aquifer.

Table 1. Statistical variables and extreme values

Elements	Standard WHO	Wet season water table				Dry season water table			
		Min	Max	Average	Standard deviation	Min	Max	Average	Standard deviation
HCO ₃ ⁻ (mg/l)	250	225	401.66	293.07	44.14	218.28	389.50	284.19	42.81
SO ₄ ²⁻ (mg/l)	250	36.1	2690	815.77	605.50	37.64	2804.92	850.62	631.37
Cl ⁻ (mg/l)	250	6.80	1770	441.77	401.05	7.09	1752.51	453.19	403.97
Ca ²⁺ (mg/l)	100	78.7	530.30	301.37	131.22	81.93	552.95	314.24	136.83
Mg ²⁺ (mg/l)	50	9.60	285.50	80.97	78.45	9.31	276.86	78.52	76.07
Na ⁺ (mg/l)	150	12.0	1252	249.89	257.00	12.51	1305.49	260.57	267.98
K ⁺ (mg/l)	12	2.00	40	9.83	7.85	2.09	33.52	9.59	6.76
pH	6.5-9.5	7.2	7.60	7.3	0.12	7.4	7.8	7.60	0.12
EC (μS/cm)	2500	550	8430	2791.97	1794.15	573.50	8790.13	2911.25	1870.7
T °C		16	22.5	18.3	1.31	16	21.4	18	1.32

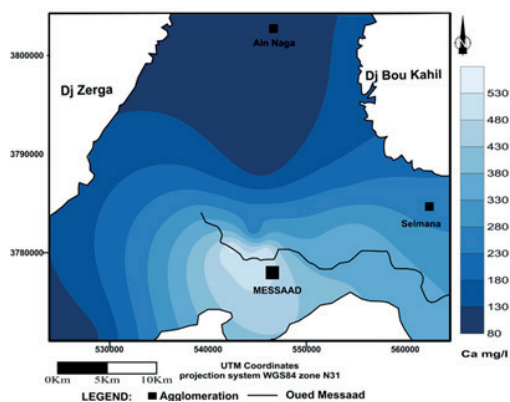
The range of variation in conductivity during all sampling campaigns varies from 550 $\mu\text{S} \cdot \text{cm}^{-1}$ to 8790.13 $\mu\text{S} \cdot \text{cm}^{-1}$. It should be noted that most samples have values greater than 2000 $\mu\text{S}/\text{cm}$. The mapping of this parameter (Fig. 4) shows that the highest values were recorded in the downstream part of the catchment area near Oued Messaad. These high concentrations can be explained by a number of reasons, including the dissolution of salt-bearing formations by the groundwater flowing downstream. In addition, the Oued Messaad is the main waterway for rainfall and domestic wastewater, and other urban discharges, which contain a considerable polluting load. In general, the chemical mapping for all the elements studied in this work clearly shows that the areas near the Oued are highly contaminated. In the majority of cases, high concentrations occur above the potability thresholds, where the mean values change in the

same way as the conductivity for all measuring points (Fig. 5–10). The representation of the water samples on the Piper diagram (Fig. 11a) indicates the tendency towards the calcium pole in the sub-triangle of the cations, while the anions show a sulphate dominance for most of the points. The distribution of major cations and anions follows a decreasing order: $\text{Ca}^{2+} > \text{Na}^+ > \text{Mg}^{2+}$ and $\text{SO}_4^{2-} > \text{Cl}^- > \text{HCO}_3^-$ (Fig. 11b). This distribution confirms the predominance of calcium sulphate and calcium chloride facies on the global Piper diagram, indicating that the mineralization of water is essentially linked to SO_4^{2-} , Cl^- and Ca^{2+} ions, and has evolved from the 2nd to the 3rd stage of chemical evolution. Second, there are two other facies, such as calcium bicarbonate and sodium sulphate. The dominance of the calcium sulphate and calcium chloride facies indicates the saliferous influence on the water chemistry of the region, indeed, the gypsum clays and the marls intercalated in the Barremian formations are at the origin of these facies.



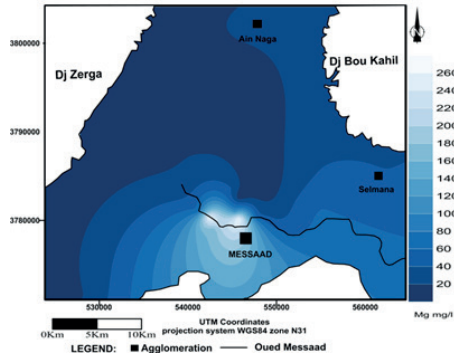
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Fig. 4. Conductivity maps: (a) wet season water table, (b) dry season water table



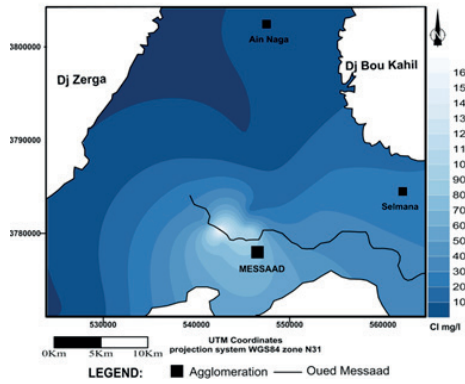
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Fig. 5. Map of calcium, July 2018



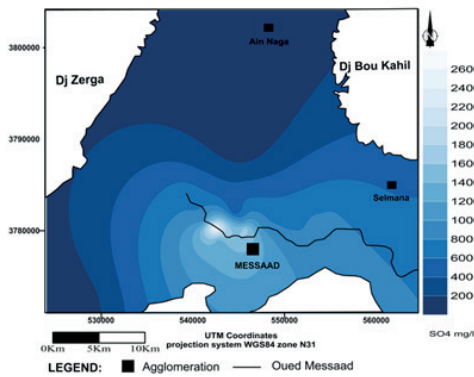
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Fig. 6. Magnesium map, July 2018



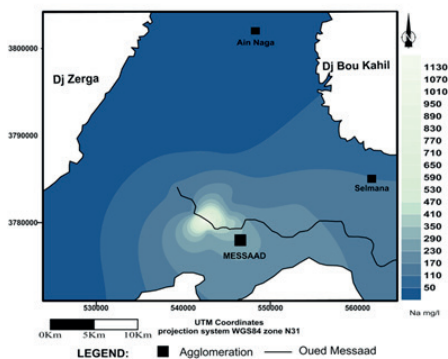
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Fig. 7. Chloride map, July 2018



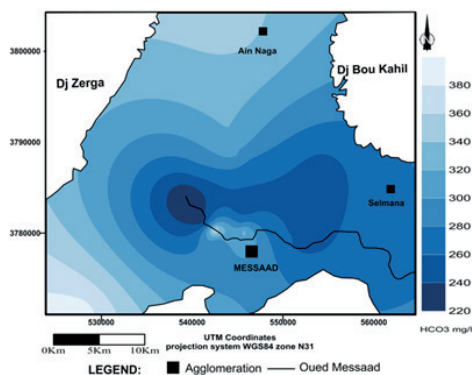
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Fig. 8. Sulphate map, July 2018



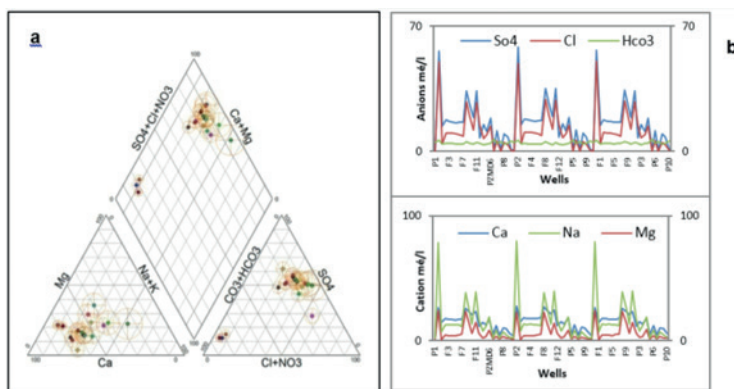
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Fig. 9. Map of sodium, July 2018



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Fig. 10. Map of bicarbonates, July 2018



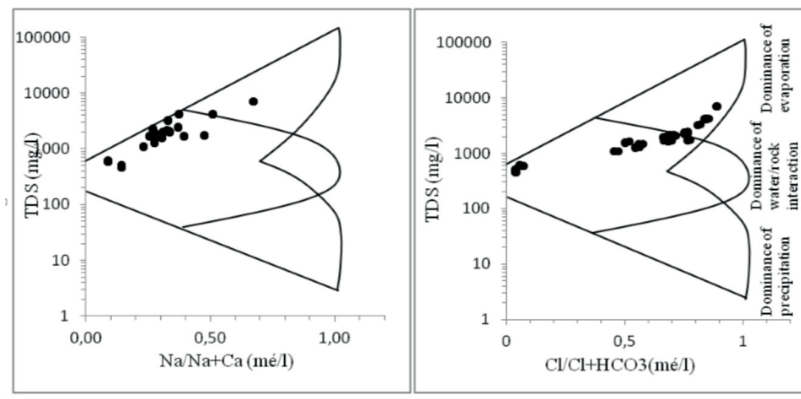
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Fig. 11. Piper diagram (a), Distribution of major elements (b)

5.1. Mechanism of acquisition of water mineralization

5.1.1. Gibbs Diagram 1970

The concentration of chemical compounds in natural groundwater depends on many processes and conditions, including mineral availability, solubility, and the geochemical environment. The Gibbs diagram summarizes the evolution of water chemistry according to three main governing processes include evaporation, precipitation, and the interaction between water and rocks. Gibbs relied on the ratios of $\text{Na}/\text{Na}^+ \text{ Ca}$ and $\text{Cl}/\text{Cl}^+ \text{ HCO}_3$ to the values of total dissolved solids (TDS). The Gibbs diagram (Fig. 12) indicates that the dominant process determining the composition of water is the interaction between water, rock and evaporation. However, examination of diagrams A and B shows a trend towards evaporation, which makes sense given the arid and dry climate conditions of the region, especially in the southern part where the static level is low 4–15 m. The evaporation of water in the unsaturated zone leads to precipitation and deposition of evaporites, which eventually leach into the saturated zone. Evaporation is not the only phenomenon in the acquisition of mineralization. Given the depth of the water, which exceeds 30 m in the recharge zone located to the north-west, evaporation is minimal. The ionic charge of the groundwater in the study area is controlled by both processes. The interaction between water and rocks in the north-west part, where the water depths are greater, and thus the phenomenon of evaporation is negligible. When one moves south-east, where the water level becomes low, a second process intervenes which is evaporation, and increases the ionic charge – this is clear in the chemical cartography.



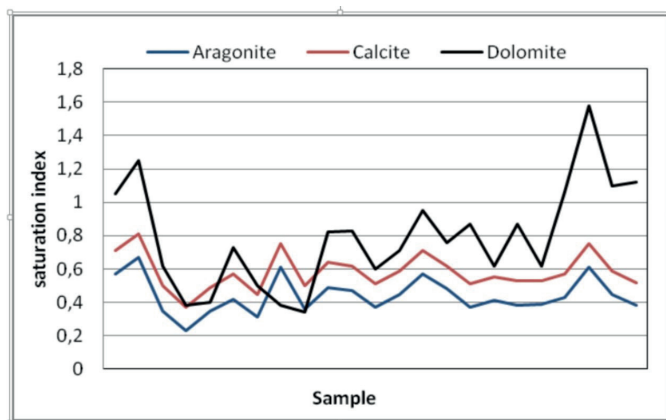
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Fig. 12. Gibbs diagram

5.1.2. Saturation indices

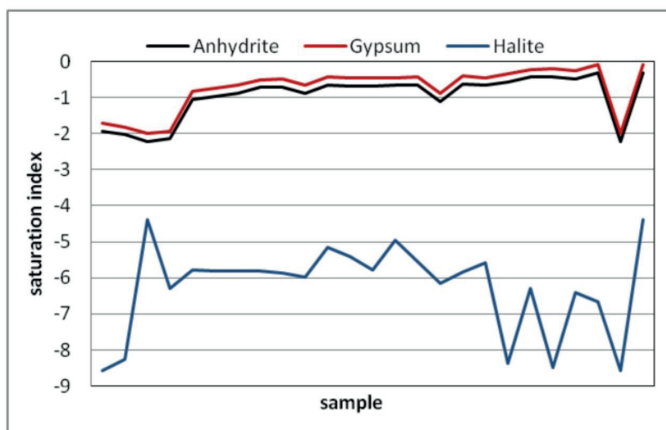
The calculation of the index for the July 2018 campaign was made by the DIAGRAMME software. The results obtained show that the carbonate minerals have positive saturation indices (Fig. 13), the index of calcite varies from +0.30 to +0.87, the aragonite

index – from +0.23 to +0.67, and the dolomite index – from +0.34 to +1.58. An over-saturation of these minerals at all sampled water points indicates that the salt load is not influenced by the water-carbonate mineral interaction. On the other hand, the evaporitic minerals present low and negative indices in all the water points sampled (Fig. 14): the gypsum index varies from -1.99 to -0.1 , the anhydrite index – from -2.21 to -0.32 and the halite index recorded very low indices between -8.56 and -4.39 . These negative values indicate an under-saturation with respect to the evaporitic minerals, the dissolution of which contributes to the acquisition of solutes and controls mineralization.



Source: Authors' own study

Fig. 13. Variation of saturation indices of the carbonate minerals

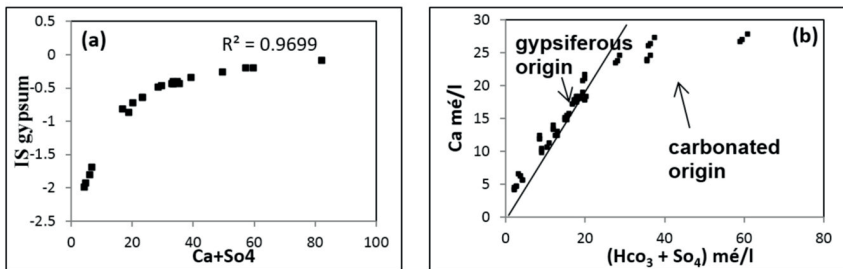


Source: Authors' own study

Fig. 14. Variation of saturation indices of the evaporitic minerals

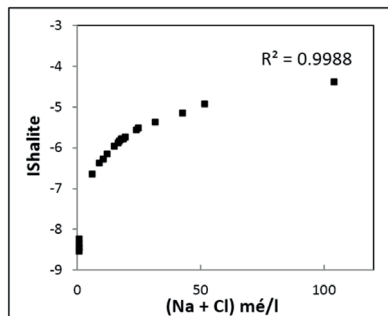
5.2. Origin of major elements

Ca^{2+} shows a very high variation in concentrations, with 80% of the wells exceeding the standards set by the WHO (standard deviation is relatively large – 131), due to the dissolution of two different rocks: gypsum clays interbedded in the Barremian formations and carbonate formations of the Jurassic and Cretaceous at the edge of the water table. This is confirmed by Figure 15, which shows the evolution of calcium as a function of bicarbonates and sulphates, where 20% of all samples have a carbonate origin. Furthermore, the close R^2 correlation between the gypsum saturation index and the concentration of $\text{Ca}^{2+} + \text{SO}_4^{2-}$ confirms that the majority of these ions have a common origin – the dissolution of the gypsum.



Source: Authors' own study

Fig. 15. Correlation of water saturation indices with gypsum as a function of $\text{Ca}^{2+} + \text{SO}_4^{2-}$

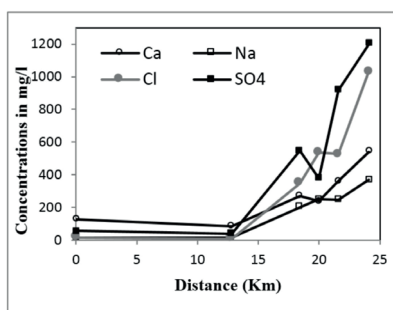


Source: Authors' own study

Fig. 16. Correlation of water saturation indices with halite as a function of $\text{Na}^+ + \text{Cl}^-$

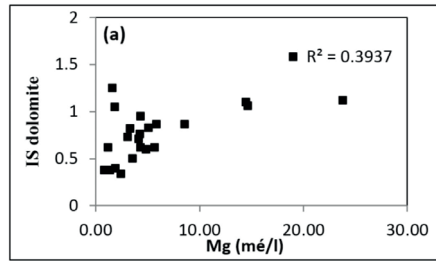
The SO_4^{2-} as the Ca^{2+} ion results from the dissolution of gypsum rocks according to the relation: $\text{CaSO}_4 \cdot 2\text{H}_2\text{O} = \text{Ca}^{2+} \text{SO}_4^{2-} + 2\text{H}_2\text{O}$. Large variations in the concentration of this element (standard deviation 605) could be explained by the lateral change in the faces of the Barremian formations from north-west to south-east [Beregh 2001]. The low values are located in the upstream part of the study area, where the ground-

water is at the beginning of its path, i.e. not yet too mineralized [Guaidia 2007]. The concentration increases as one moves towards the accumulation zone in the south-east part, where the terrains become more clayey [Beregh 2001]. Cl^- and Na^+ show very high concentrations, exceeding the standards set by the WHO in 80% of the wells and showing the same values as SO_4^{2-} and Ca^{2+} . The origin of the Cl^- and Na^+ ions in the groundwater of the study area is the dissolution of the NaCl rich formations (clay and marl), which is confirmed by the important correlation between Cl^- and Na^+ (0.94) and the close correlation between the halite saturation index and the concentration of $\text{Cl}^- + \text{Na}^+$ (Fig. 16). The concentrations of the SO_4^{2-} , Ca^{2+} , Cl^- and Na^+ elements, which have the largest influence on the electrical conductivity, increase according to the direction of flow from north-west to south-east, so that the water is gradually loaded by dissolution of the formations rich in halite and gypsum (Fig. 17). K^+ results from the alteration of the potassium clay and the dissolution of chemical fertilizers used by the farmers on the side of the Messaad Oued where concentrations of this ion reach its maximum 40mg/l. Mg^{2+} shows a low variation in content (standard deviation 78), with the exception of some wells near the Oued, which have very high levels exceeding the potability standards. The sewage in the Oued may be the cause for that. The low R^2 correlation between the dolomite saturation index and the concentration of Mg^{2+} (Fig. 18) confirms that the evolution of this ion content in the waters of the study area is linked to the dissolution of the evaporative minerals (MgSO_4 , MgCl). This is confirmed only by the strong correlations that exist between these ions: Mg^{2+} vs SO_4^{2-} (0.84), Mg^{2+} vs Cl^- (0.92). However, the high values of these ions in wells P2, F8, F9 and F11, SO_4^{2-} [1267,5–2690] mg/l, Cl^- [710–1770] mg/l, Ca^{2+} [465–530] mg/l, Na^+ [265–1252] mg/l, with EC [4200–8430] $\mu\text{s}/\text{cm}$, assumes possible anthropogenic pollution of the water by domestic wells, which are located very close to the Messaad Oued, where the wastewater discharged directly into the Oued can infiltrate and contaminate the water table [Henri 1971]. In addition, domestic waste is thrown indiscriminately and directly into the Oued, where it is exposed to rainwater and produces a liquid fraction called leachate (also known as percolate). It can contaminate the water table and surface water [Emilien 2009].



Source: Authors' own study

Fig. 17. Evolution of elements SO_4^{2-} , Ca^{2+} , Cl^- and Na^+ next NW-SE groundwater flow direction



Source: Authors' own study

Fig. 18. Correlation of water saturation indices with dolomite as a function of Mg^{+}

6. Conclusion

The study area in the Messaad plateau is part of the arid zones. It includes the Barremian aquifer that functions as a supply of the domestic and the irrigation water. The conclusions of this paper on the quality of the groundwater are the following: the samples of water from the wells have very high conductivity values indicating high mineralization, as most of the chemical parameters are higher than the standard of the WHO potability, and some wells are above the standard. The spatial distribution of the conductivity values and the various chemical parameters clearly reveal that the area near the Messaad Oued is highly mineralized with a predominance of calcium sulphate and calcium chloride facies.

Groundwater chemistry is primarily related to the lithological contamination of the Barremian aquifer. These salt-bearing layers have an essential role in the mineralization of the water table. The used graphs of the origin of the main major elements influencing electrical conductivity indicate the role of the ions Ca^{2+} and SO_4^{2-} derived from the dissolution of continuous gypsum in the Barremian formations. Ca^{2+} is also produced by the dissolution of the carbonate formation, especially in the north-west of the region. The ions Na^{+} and Cl^{-} originate from the dissolution of the continuous halite in the marls and clays, especially in the south-east of the region. These ions cause the increase in the conductivity of the water along the north-west to south-east axis.

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Conflict of interest statement

On behalf of all authors, the corresponding author states that there is no conflict of interest. All participating authors, have no a financial or personal relationship with any third party whose interests could be positively or negatively influenced by the article's content.

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