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HYDROGEOCHEMICAL CHARACTERIZATION OF GROUNDWATER IN THE TERMINAL COMPLEX AND INTERCALARY CONTINENTAL AQUIFERS, OUARGLA, SOUTHEASTERN ALGERIA

Abstract: Groundwater is a crucial resource in arid and semi-arid regions, particularly in Ouargla province, southeastern Algeria, where extreme aridity and chronic water shortages prevail. This study investigates the geochemical processes shaping groundwater quality within two major aquifer systems: the Terminal Complex (TC) and the Intercalary Continental (IC). A multidisciplinary approach was applied, including physicochemical analysis of water samples, hydrochemical facies classification using the Chadha diagram, correlation of major ions, evaluation of mineral saturation indices, and calculation of the Base Exchange Index (BEI). The findings highlight that evaporate dissolution, mainly of halite and gypsum, is the dominant process controlling mineralization. This is reflected in elevated levels of chlorides, sulfates, and sodium in groundwater. Chadha diagram results revealed diverse hydrochemical facies, with Ca-Mg-SO_4 and Ca-Mg-Cl types prevailing, along with a significant Na-Cl signature in the TC aquifer. Cation exchange between groundwater and clay minerals was also identified as an essential mechanism, responsible for sodium enrichment and calcium depletion in several samples, as confirmed by BEI values. Saturation index analysis demonstrated under saturation with respect to halite, gypsum, and anhydrite, supporting their active dissolution, while waters were supersaturated with calcite and dolomite, indicating potential precipitation. Overall, the study concludes that groundwater chemistry in Ouargla is primarily governed by natural mineralization processes and ion exchange reactions. These insights are fundamental for the sustainable management of groundwater resources, particularly for irrigation and other vital uses in this highly water-stressed region.

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Introduction

As demand for reliable, high-quality water supplies increases, and surface water becomes scarce, groundwater is one of the most important freshwater resources in arid and semi-arid regions. The sustainability of these vital aquifers is increasingly threatened by natural factors such as mineral dissolution, and human pressures including over-extraction and pollution (Rajan et al., 2024). Beneath the vast stretches of the Sahara lies one of the world's most strategically vital and most vulnerable water reserves. The North-Saharan Aquifer System (NSAS) is the primary, and often the only, dependable source of water for more than 30 million people across Algeria, Tunisia, and Libya (Rachid, 2025). However, intensive groundwater abstraction, and prolonged arid climatic conditions have led to significant deterioration in groundwater quantity and quality throughout the region. This threatens the long-term sustainability of these strategic underground reservoir systems.

This situation is clearly evident in the Ouargla Basin of southeastern Algeria, where the average annual rainfall barely reaches 40 mm, and the evaporation rate exceeds the rainfall rate by sixty times (Slimani et al., 2021; Medjani et al., 2023; Ferhat and Saidou, 2025). Groundwater resources in the area are mainly derived from two major aquifer systems: the Intercalary Continental (IC) and the Terminal Complex (TC). These aquifers support a rapidly growing population, expanding urban areas, and extensive irrigated agriculture dominated by date-palm cultivation. At the same time, the hydrogeological setting of the Ouargla depression promotes saline recharge from surrounding chotts and evaporitic formations, resulting in naturally elevated salinity and complex hydrochemical processes even before anthropogenic influences are considered (Maha et al., 2024; Kumar et al., 2025). The hydrogeological picture in the Ouargla region is still incomplete, as previous studies have been limited either to a narrow local scale, to low spatial resolution, or to oil field monitoring data (Bouziane et al., 2025). Addressing this knowledge gap is essential for developing effective water management strategies that safeguard both current and future water security under intensifying climatic and socioeconomic challenge.

Hydrogeochemical characterization of groundwater is essential for understanding the origin, evolution, and suitability of water resources, particularly in arid and semi-arid regions where groundwater often serves as the primary supply (Lakhdar et al., 2026). This process involves detailed analysis of physicochemical parameters such as pH, electrical conductivity, total dissolved solids, and major ion concentrations like Ca^{2+}, Mg^{2+}, Na^{+}, K^{+}, Cl^{-}, SO_4^{2-}, HCO_3^{-} (Gao et al., 2020; Wang et al., 2015). Graphical methods like Piper, Chadha, and Gibbs diagrams are commonly employed to classify water types and infer the dominant geochemical processes, including mineral dissolution, cation exchange, evaporation, and anthropogenic influences (Jaramillo-Colorado et al., 2025). Saturation indices help assess equilibrium conditions between groundwater and aquifer minerals, while multivariate statistical techniques aid in identifying spatial patterns and source contributions. Collectively, these methods provide critical insights into groundwater quality, salinization trends, and long-term sustainability, informing effective water management and protection strategies (Wang et al., 2025). The Chadha diagram it helps identify the dominant geochemical processes such as ion exchange or water–rock interaction. This diagram provides a clear visual interpretation of groundwater chemistry for hydrogeological assessments (Ghosh & Jha, 2023).

Several studies conducted across Algeria have demonstrated the effectiveness of combining hydrochemical analyses, water quality indices, and spatial approaches for groundwater assessment. Tiaiba et al. (2025) applied spatio-temporal WQI analysis and GIS mapping in the K'sob watershed to identify zones suitable for drinking-water exploitation. Abaidia et al. (2025) evaluated groundwater suitability for irrigation in the Middle Cheliff Plain using integrated hydrochemical indices. In northeastern Algeria, Nadjai et al. (2025) combined hydrochemical analyses, GIS, and WQI methods to investigate groundwater quality in Oum El Bouaghi, highlighting the influence of salinity and anthropogenic activities. Similarly, Bettahar and Şener (2024) investigated the Quaternary aquifer of Oued Souf and identified evaporite dissolution and cation exchange as dominant hydro geochemical processes controlling groundwater mineralization. Additional studies conducted in the Mitidja Plain and the Ain-Sefra region further demonstrated the importance of spatial statistics, hydrochemical faceis analysis, and geochemical modelling for understanding groundwater quality evolution in arid and semi-arid environments (Dougha and Hasbaia, 2019; Selmane et al., 2022; Aziez et al., 2025; Hamma et al., 2025).

Despite these important contributions, comprehensive basin-scale investigations integrating multiple aquifer systems remain limited in hyper-arid Saharan environments such as Ouargla. Previous studies focused on localized sectors, individual aquifers, or limited hydrochemical parameters, while large-scale assessments of hydrochemical interactions between the Mio-Pliocene Terminal Complex and the Albian-Aptian Intercalary Continental aquifers remain scarce. Furthermore, few studies have combined detailed hydrochemical characterization with geochemical interpretation methods to identify the principal mechanisms responsible for groundwater salinization across the entire Ouargla basin.

The novelty of this study lies in its provision of the first comprehensive, basin-scale, multi-aquifer assessment of groundwater quality in the Ouargla region, a hyper-arid Saharan setting facing growing water-security challenges. Unlike previous fragmented or localized investigations, this research integrates a dense network of 40 production wells across both the Mio-Pliocene Terminal Complex (TC) and the Albian–Aptian Intercalary Continental (IC) aquifers. It combines high-resolution physicochemical analyses with advanced geochemical tools. The study aims to classify hydrochemical facies, identify dominant salinization mechanisms, quantify the roles of evaporite dissolution, carbonate equilibria, and base-exchange reactions, and evaluate groundwater suitability for irrigation and drinking according to international standards. The results are expected to contribute to a better understanding of groundwater evolution in Saharan aquifer systems and to support sustainable water-resource management under increasing climatic and anthropogenic pressures.

Data and methods

Study area

Ouargla province, located in southeastern Algeria about 790 km from Algiers, spans a vast area of 211,980 km² and lies in the heart of the Sahara (Fig 1). It is bordered by several provinces including Biskra, Tamanrasset, Djelfa, Ghardaïa, El Oued, Illizi, and shares a boundary with Tunisia (Nezli et al., 2007). The province is situated in a natural depression, particularly in the Oued M'ya basin, and forms part of the Lower Sahara within the Saharan Platform. Its climate is arid and desert-like, characterized by extremely high summer temperatures, often-exceeding 50°C, and very low annual rainfall, making it one of the hottest regions in the world. Winters are mild, and the area experiences frequent sandstorms and

dry winds. In 2020, the population was estimated at 849,672 with a low density of 4 inhabitants per km². The ancient Precambrian Shield, marks the region's geology rich in metamorphic and eruptive rocks, mainly found in the Hoggar and Eglab massifs. Ouargla also sits above major aquifer systems like the Intercalary Continental and Terminal Complex. These aquifers, shared with Tunisia and Libya, are vital water sources for agriculture and human use (Fig 2a). Overall, Ouargla's harsh climate, vast desert terrain, and water resources shape its unique environmental and socio-economic conditions (Maha et al., 2024a).

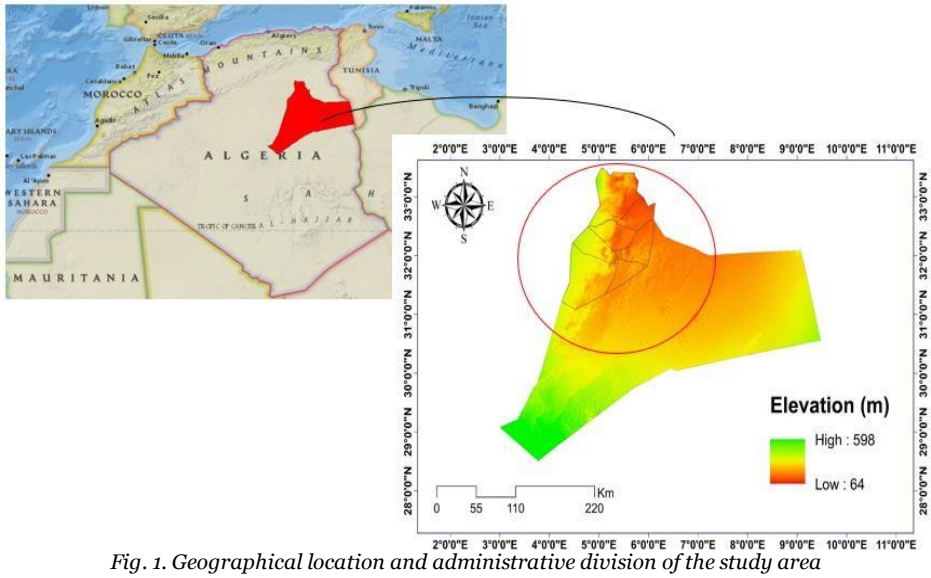


Fig. 1. Geographical location and administrative division of the study area

The IC is an aquifer extending from north to south, from the Saharan Atlas to the Tassili of Hoggar, and from west to east, from the valley of Guir and Saoura (Bechar) to the Libyan Desert (see Fig 2a). It occupies sandy and clay-sandstone soils of the Neocomian, Barremian, Aptian, and Albian, at a depth ranging between 900 and 1400 m in the study area (Maha et al., 2024b) (Fig 2b). Its water supply comes from the Piedmont of the Saharan Atlas in the northwest with a flow rate of 7.7 m^3/s, from Tinrhert in the south, Dahar in the east, Jebel Nafusa in the northeast, and Jebel Hassawna in the south (Maha et al., 2024b). The Continental Terminal aquifer, originally defined as Mio-Pliocene sandy-clayey formations, is now seen as a system linked to older Eocene, Senonian, and Turonian layers across the Sahara, its depth ranges between 100 and 200 meters in the study area. (Fig 2b) (Edmunds et al., 2003). In Ouargla, the hyper-arid climate features very low rainfall (~39 mm/year) and high temperatures, especially in July and August. Evaporation greatly exceeds precipitation, with evapotranspiration about 60 times higher. This results in a severe and constant water deficit throughout the year (Mulla et al., 2002; Guendouz et al., 2003).

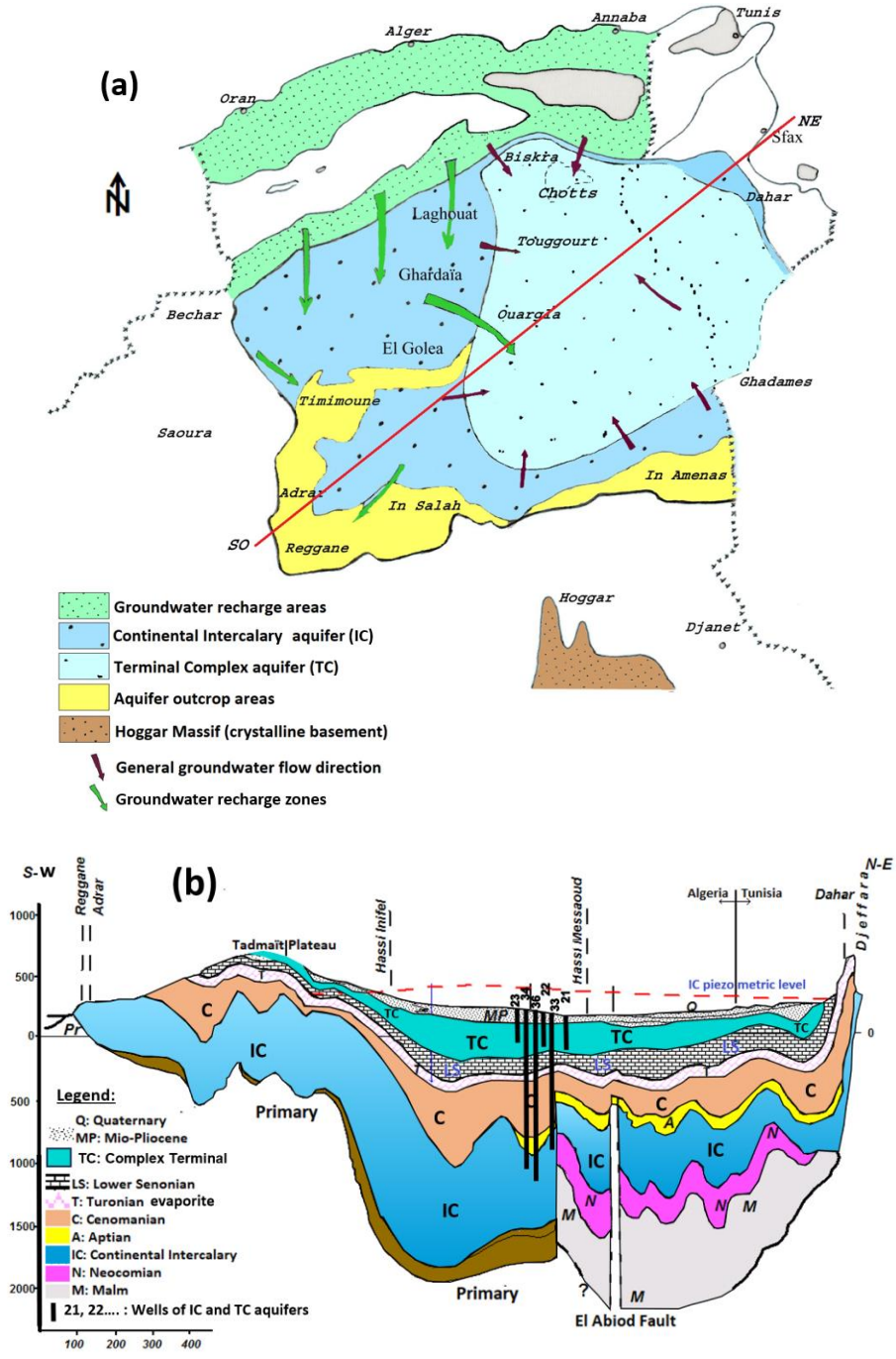


Fig. 2. Hydrogeological sketch (a) and cross-section (b) of the IC and TC aquifer system

Source: UNESCO, 1972

Sampling and collecting

Water samples collected from different wells situated in the Mio-Pliocene (TC) and Albian (IC) aquifers in Ouargla region, for analysis of major water quality parameters the conventional sampling protocol's methods were followed (Wilde 2010) (Table 1).

Twenty-seven wells from TC aquifers and eleven wells from IC aquifers (Fig 3), all of these samples were directed to the human and agricultural use.

Although microbiological analysis provides direct evidence of biological contamination and health risks, this study did not employ microbiological analyses. Instead, it relied on physical, chemical, and hydrochemical parameters because these provide valuable information about mineralization processes, water-rock interactions, salinity sources, and general hydrochemical properties.

Table 1. Results of physicochemical analyses of selected wells in the region of Ouargla.

Element	Unit	Mio-Pliocene Water (TC)			Water Albian (IC)		
		Max	Min	Aver	Max	Min	Aver
EC	mS/cm	6.52	4.14	4.99	3.84	2.33	2.93
DR	g/l	6,11	2.11	3.96	3.04	1.50	2.27
pH		8.10	6.62	7.67	8.37	7.22	8.00
Na^+	meq/l	40.52	17.43	29.19	19.02	8.02	12.03
K^+		1.13	0.24	0.58	1.13	0.36	0.52
Ca^{2+}		26.45	10.88	17.62	9.44	5.54	7.55
Mg^{2+}		29.65	7.90	16.16	9.09	3.76	5.40
HCO_3^-		3.44	0.25	1.83	3.70	0.71	1.82
Cl^-		57.68	15.50	34.98	18.31	10.31	15.39
SO_4^{2-}		30.21	6.77	15.51	10.21	5.07	7.89

Note: EC: electrical conductivity, DR: dry solids

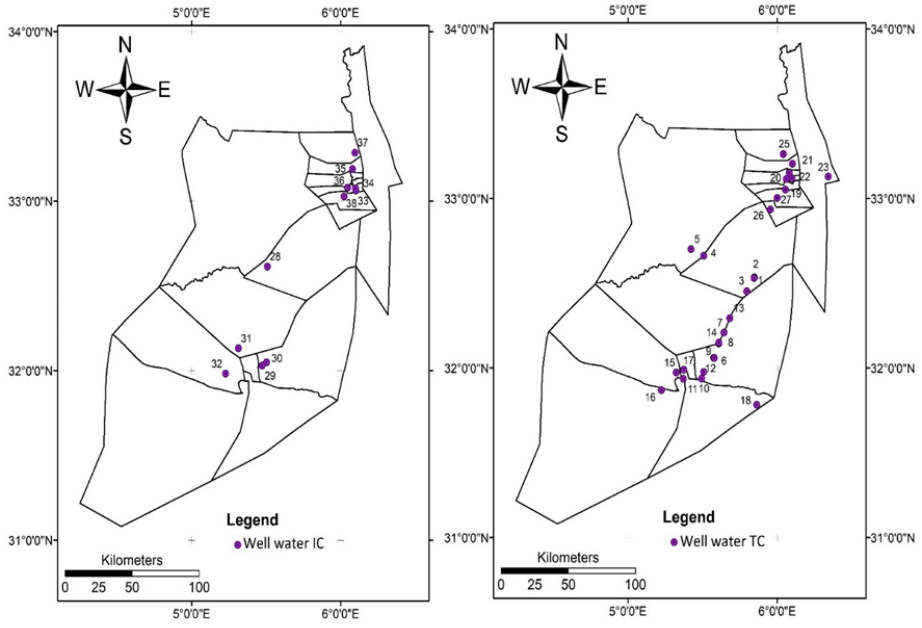


Fig. 3. Geographic distribution of water wells studied for IC and TC in the Ouargla region

Results and discussion

Chadha Diagram Analysis

To explain the hydrochemical processes governing mineralization in a multilayered aquifer system and to classify groundwater analytical data into different water types, the Chadha diagram (Chadha, 1999) is used. The Chadha diagram is essentially a modified form of the Piper and Durov diagrams with an expanded classification system (Nagaraju et al., 2016). Chadha diagram (Fig 4) illustrating the hydrochemical facies distribution of groundwater in the Mio-Pliocene (TC) and Albian (IC) aquifers of the Ouargla region. Plotting the analytical results of the two studied aquifers reveals distinct hydrochemical facies. Groundwater from the Mio-Pliocene aquifer (TC) presents two major facies: the first is dominated by alkaline-earth metals (Ca^{2+} + Mg^{2+}) exceeding 66%, corresponding to a Ca-Mg-SO_4 or Ca-Mg-Cl water type, with strong anions (Cl^- and SO_4^{2-}) prevailing over weak anions (HCO_3^- and CO_3^{2-}), and a clear dominance of alkaline-earth cations over alkali metals (Na^+ and K^+). The second facies are defined by a predominance of alkali metals (Na^+ + K^+) over 33%, representing a Na-Cl water type, where sodium and chloride play a major geochemical role. In contrast, groundwater from the Albian aquifer (IC) predominantly exhibits a single facies-Ca-Mg-SO_4 or Ca-Mg-Cl-accounting for 99% of the samples. This hydrochemical classification is instrumental in understanding the water–rock interactions, ion exchange mechanisms, and potential mineralization sources governing the groundwater quality in the Ouargla region.

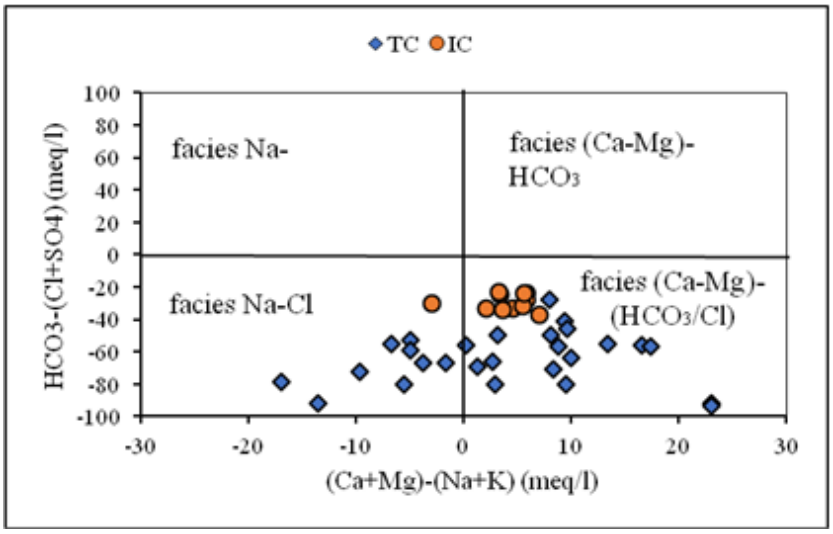


Fig. 4. Chadha Diagram Showing Hydrochemical Facies Distribution of Groundwater in the Mio-Pliocene (TC) and Albian (IC) Aquifers of the Ouargla Region

Halite dissolution is typically observed in sodium-chloride-type waters. In contrast, the simultaneous dissolution of halite and gypsum is indicated in water types where the concentration order is chloride > sulfate > calcium > sodium. Notably, sodium (Na^+) concentrations decrease due to cation exchange processes, while calcium (Ca^{2+}) concentrations increase. This exchange leads to elevated groundwater saturation with respect to Ca^{2+}, which subsequently reduces gypsum dissolution. This activity guarantees that chloride concentration exceeds that of sulfate because of the conservative nature of chloride as an element. Furthermore, the ongoing

utilization of sodium in cation exchange renders the groundwater increasingly under-saturated with respect to halite, thereby promoting its dissolution (Hamed et al., 2011).

Correlations between major parameters

Sulfates and bicarbonates

Sulfates (SO_4^{2-}) are one of the most pervasive elements that take place in natural aquatic systems. They exist in their oxidized state and are present in some evaporitic sediment, like gypsum ($CaSO_4 \cdot 2H_2O$), and mineral forms of barite ($BaSO_4$) and anhydrite ($CaSO_4$). In anoxic conditions, the predominant species in groundwater is sulfate ions (SO_4^{2-}) that are in close association with the redox characteristics of the environment (Ward & Fox, 2012). In the TC and IC aquifers examined, sulfate ions constitute the predominant hydrochemical facies. The primary source of sulfate ions in the water bodies is evaporitic formations. Sulfate ions are retained from the groundwater movement through these formations by anhydrite and gypsum dissolution reactions. The bivariate plots of sulfate against of the other contents (Ca^{2+}; Mg^{2+}; Na^+ and is of gypsum) indicates that the correlation coefficient R^2 varies between 0.19 and 0.72, the highest coefficient is recorded between the sulfate and the gypsum, on the other hand the Na^+ that records the slightest correlation ($R^2 = 0.19$) with sulfates in the Mio-Pliocene water table. Were showed that a low value of correlation coefficient of sulfate and calcium ($R^2 = 0.21$) in the Albian water table. Generally, we can say that sulfates have a good correlation with Cg^{2+}; Mg^{2+}; Na^+ and is gypsum.

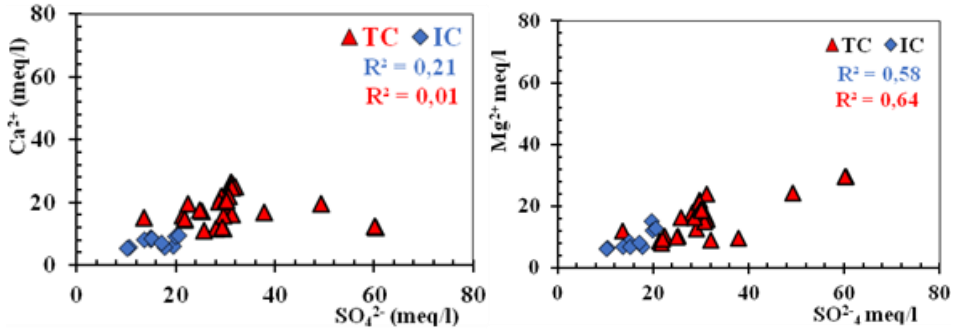


Fig. 5. Bivariate plots of SO42- against Mg2+ and SO42- against Ca2+

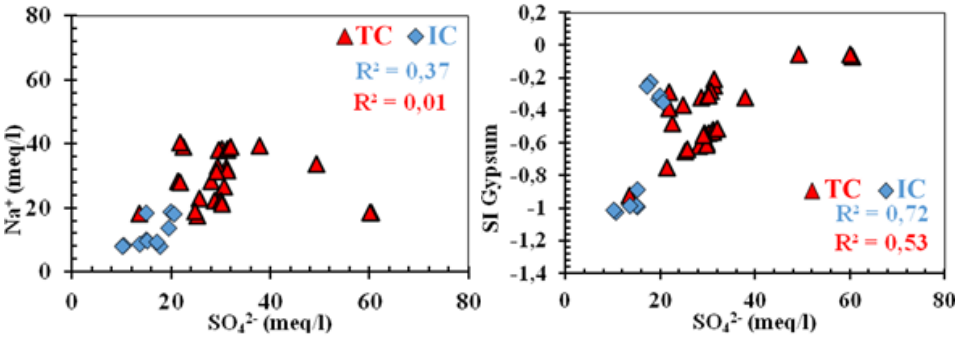


Fig. 6. Bivariate plots of SO42- against Na+ and SO42- against SI of gypse

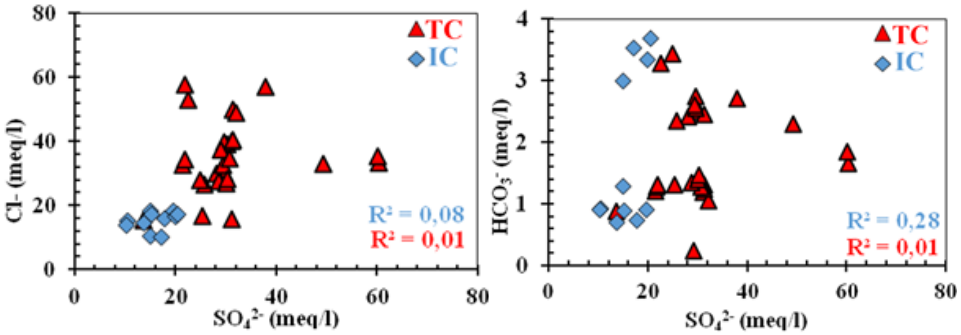


Fig. 7. Bivariate plots of SO42- against Cl- and HCO3-

Figs 5, 6, 7, and 8 illustrate bivariate plots of the parameters. Fig 5 presents bivariate plots illustrating the relationships between SO_4^{2-} and Mg^{2+}, as well as SO_4^{2-} and Ca^{2+}, in groundwater sample.

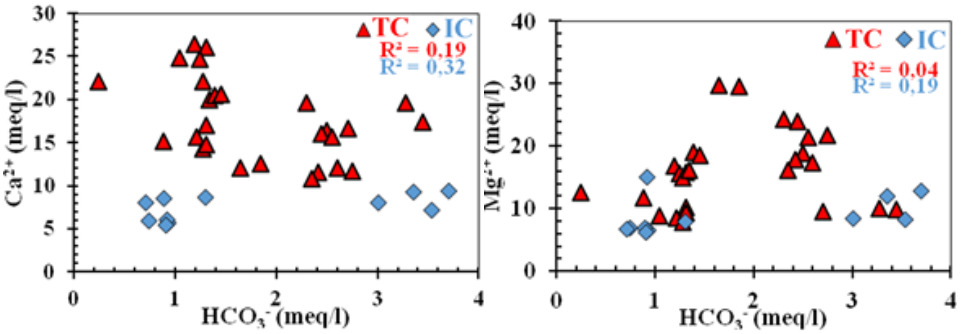


Fig. 8. Bivariate plots of HCO3- against Ca2+ and Mg2+

A weak correlation between sulfate and either chloride or bicarbonate concentrations (Fig 8) indicates that these anions are controlled by different processes. When bicarbonate and sulfate are plotted against calcium and magnesium, most samples cluster along trends consistent with evaporite rather than carbonate dissolution, confirming that halite and gypsum are the dominant mineral sources in both the Mio-Pliocene (TC) and Albian (IC) aquifers. Chloride and sulfate levels are generally high: 59.3% of TC samples and more than 45% of IC samples have SO_4^{2-}/Cl^- ratios below 1, reflecting a chloride excess, whereas ratios ≥ 1 identify sulfate-rich waters in which simultaneous gypsum and halite dissolution elevates salinity The waters studied form a bipolar assemblage of water points (Halassa et al., 2019). In the (SO_4^{2-}/Cl^-) versus ($1/Cl^-$) diagram, a significant portion of the samples are located in a pole characterized by the lowest $1/Cl^-$ ratios and a pole represented by the highest SO_4^{2-}/Cl^- ratios. Fig 9 presents bivariate plots showing the relationship between (SO_4^{2-}/Cl^-) and ($1/Cl^-$), as well as between (SO_4^{2-}/Cl^-) and ($1/Ca^{2+}$) in groundwater sample.

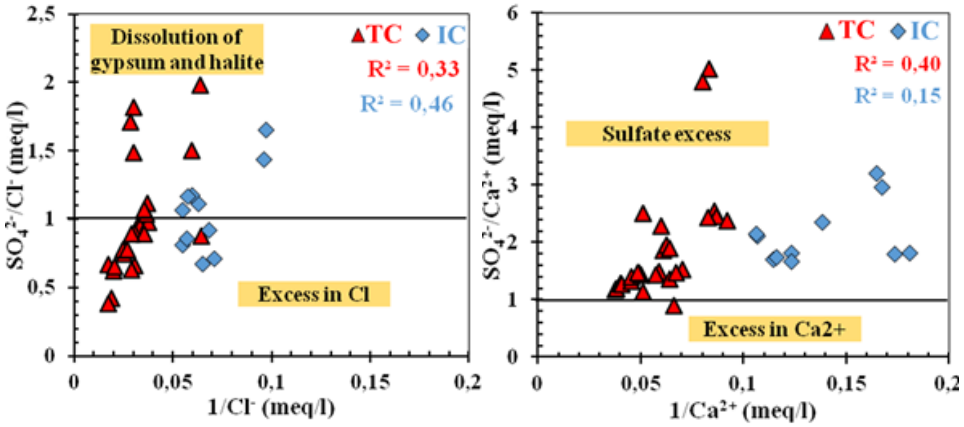


Fig. 9. Bivariate plots of (SO42−/Cl−) against (1/Cl-) and (SO42−/Cl−) against (1/Ca2+)

The projection of SO_4^{2-}/Ca^{2+} versus $1/Ca^{2+}$ reveals that most data points fall in a zone where the SO_4^{2-}/Ca^{2+} ratio exceeds 1, indicating a dominant sulfate presence in both the Mio-Pliocene (TC) and Albian (IC) aquifers. This sulfate dominance suggests that evaporite mineral dissolution, particularly of gypsum and magnesium sulfate, is the principal source of these ions, as supported by Fig 9. a subset of samples displays SO_4^{2-}/Ca^{2+} ratios near or below 1, likely due to cation exchange processes within clay minerals (Halassa et al., 2019). The absence of calcium excess in these samples implies that calcium contributions may also stem from limited calcite dissolution, reinforcing the complex interplay between evaporite and carbonate sources in shaping groundwater chemistry.

3.2.2 Chloride and sodium

Chloride and sodium in groundwater chiefly derive from halite dissolution and, to a lesser extent, from evaporation within endorheic basins. As halite (NaCl) dissolves, it releases Na^+ and Cl^-, making chloride a reliable tracer for salinity evolution because it is highly soluble, chemically conservative, and largely unaffected by redox reactions or microbial processes (Ribeiro dos Santos, 2017). Consequently, variations in Na^+ concentrations plotted against chloride provide valuable insight into ion sources and water–rock interactions, enabling discrimination between simple evaporate dissolution and more complex processes such as cation exchange or mixing with less mineralized waters. Fig 10 illustrates bivariate plots of Cl^- against $(Na^+ + K^+)$ and Cl^- against Na^+. Fig 10 presents bivariate plots illustrating the relationship between Cl^- and $(Na^+ + K^+)$, as well as between Cl^- and Na^+ in groundwater samples.

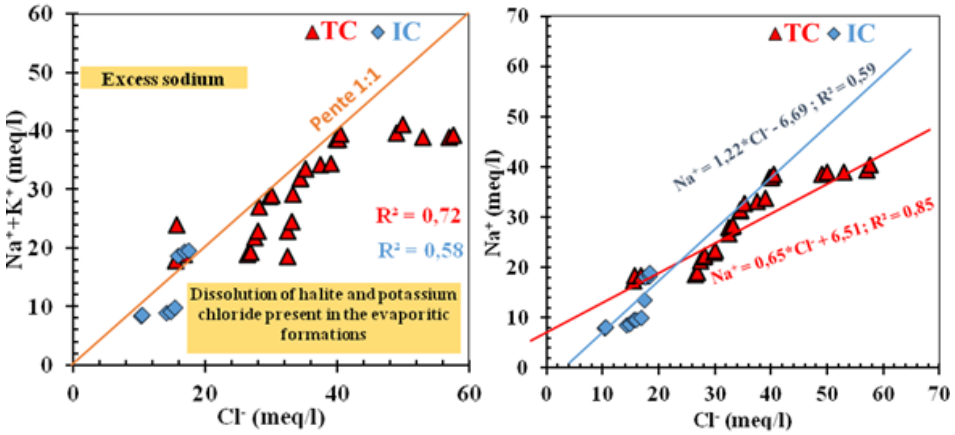


Fig. 10. Bivariate plots of Cl– against (Na++K+) and Cl– against Na+

The high Na^+, K^+ and Cl^- contents may be due to the dissolution of halite in addition, potassium chloride contained in the evaporate formations. The projection of the sum of (Na^++K^+) concentrations as a function of chloride concentrations Fig 10 indicates a good correlation between them. The largest percentage of samples for both aquifers is found below the slope 1 line, in the zone of dissolution of halite and potassium chloride. On the other hand, the lowest percentage is recorded for samples characterized by an excess of sodium, which reflects on the one hand the dominance of chloride over sodium and potassium and on the other hand, the existence of other origins such as ionic exchanges within the clays between monovalent (Na^+, K^+) and divalent (Ca^{2+}, Mg^{2+}) cations. The combined presence of carbonate formations and silty clays in the geological context of theTC aquifer may promote such an exchange. This is particularly true for basic exchanges (Ca^{2+} vs. Na^+), or the hydrolysis of silicates in sandstones and clays (Halassa et al., 2019).

The concentrations of these two elements are extremely high in the Mio-Pliocene water especially at well No. 22 in the municipality of Zaouïa Abidia, and it is the most excessively saline of all the wells (6.11 g/l salinity). Conversely, the water from well No. 31 located in the municipality of Hassi Ben Abdallah has the least saline water. The relationship between these two elements is characterized by a good correlation coefficient of R^2 = 0.85. For Albian waters, the relationship between chloride and sodium is less correlated compared to the Mio-Pliocene aquifer (R^2 = 0.59).

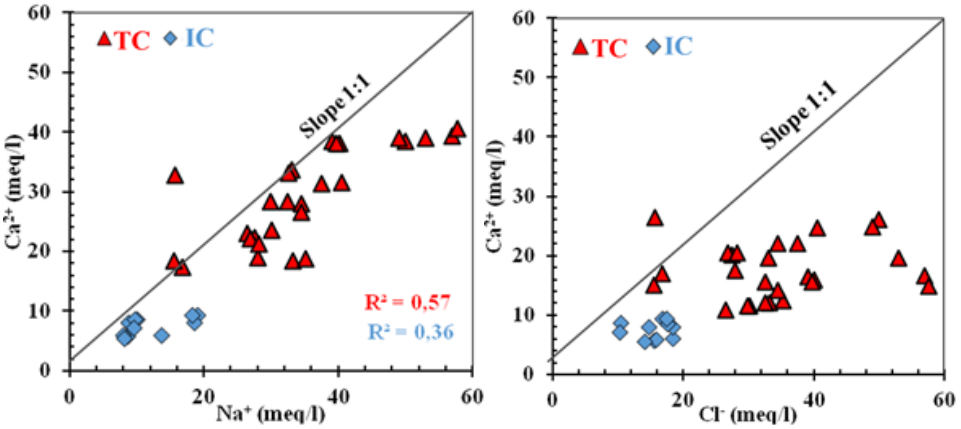


Fig. 11. Correlations between Ca^{2+} and Na^{+} in Groundwater Irrigation Waters in the Ouargla Region

The study of the variation of Ca^{2+} as a function of Na^{+} (Fig 11) indicates that the majority of water points are characterized by excess sodium, this excess increases with the mineralization of the water. Other points are located on the straight line of slope 1, and a few water points are characterized by excess calcium relative to sodium. This variation is mainly due to the participation of Ca^{2+} ions in cation exchange processes with clay minerals. Fig 11 illustrates the correlation between Ca^{2+} and Na^{+} in Groundwater Irrigation Waters in the Ouargla Region.

The excess of Na^{+} can be explained by the cation exchange reaction, which occurs between the rich waters by Na^{+} and the sediments of the two aquifers studied, according to the equation below (Appelo and Postma 1993):

$$Na^{+} + \frac{1}{2}Ca - X \rightarrow Na - X + \frac{1}{2}Ca \quad (1)$$

where X indicates the sediment exchanger.

According the Fig 11 reveals a weak correlation between these two elements, as most groundwater samples intended for agricultural use in the Ouargla region consistently show Ca^{2+} concentrations lower than those of Cl^{-}. This lack of correlation is both logical and expected, given that calcium and chloride are rarely directly associated in groundwater geochemical reactions. Their poor correlation, particularly at both low and high concentrations, suggests that distinct processes control their respective behaviors. The observed variability in their concentrations is most likely linked to the dissolution of evaporitic minerals rather than a shared geochemical pathway.

The bivariate plots of the (Na^{+}/Cl^{-}) ratio against the $(Ca^{2+}/(HCO_3^{-} + SO_4^{2-}))$ ratio, as shown in Fig 12, confirm the occurrence of cation exchange processes. In this diagram, the samples influenced by cation exchange exhibit a noticeable calcium deficit accompanied by an excess of sodium. This geochemical signature strongly supports the exchange of Ca^{2+} ions in the groundwater with Na^{+} ions adsorbed onto clay minerals, a common phenomenon in sedimentary aquifers subjected to long water–rock interaction. Fig 12 illustrates the chemical process of cation exchange in the IC and TC aquifers within the Ouargla region.

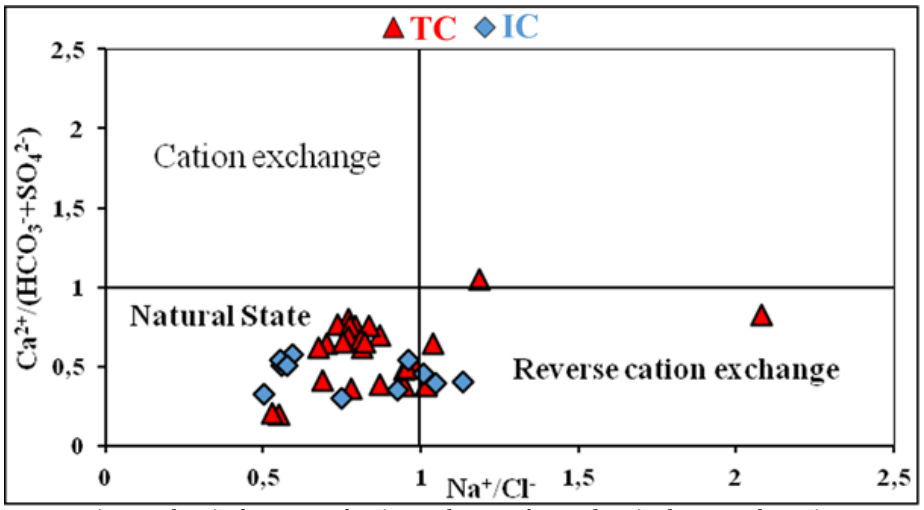


Fig. 12. Chemical process of cation exchange of IC and TC in the Ouargla region

3.2.3. Correlation of EC with major anions

The groundwater of Mio-Pliocene aquifer are characterized by a remarkable richness in chlorides and sulfates relative to carbonate anions (HCO_3^-). The excessive mineralization of the waters is due to the abundance of these two evaporate anions. We can see in the diagram presented in Fig 13.a, shows a good significant correlation (-0.82) between the decrease in the ratio ($[HCO_3^-]/ [Cl^- + SO_4^{2-}]$ and the increase in EC.

The major anions within the Albian aquifer are present in excess. Sulfates and chlorides predominate in the waters while bicarbonates remain relatively low. The groundwater of Albian aquifer has excessive mineralization, but less pronounced compared to the waters of the Terminal Complex aquifer. The recorded EC values range between 2330 and 3840 µS/cm. Fig 13.b shows a strong negative correlation (R^2 = -0.63) between the decrease in the ratio $[HCO_3^-]/[Cl^- + SO_4^{2-}]$ and the increase in EC. Fig 13 illustrates the relationship between electrical conductivity (EC) and the carbonate/evaporate ratio in irrigation waters of the Ouargla region (a: Mio-Pliocene aquifer; b: Albian aquifer).

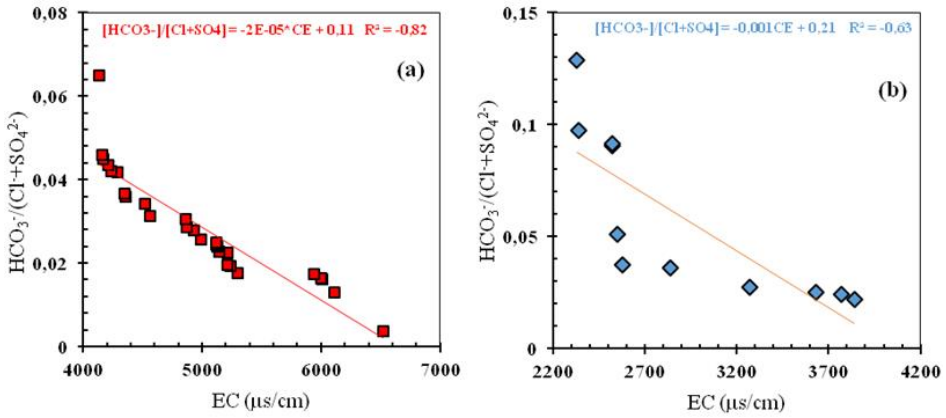


Fig. 13. The relationship between electrical conductivity (EC) and the carbonate/evaporite ratio in irrigation waters in the Ouargla region (a: Mio-Pliocene aquifer; b: Albian aquifer)

In the Mio-Pliocene aquifer, most samples display a clear chloride surplus relative to sulfate; this dominance becomes pronounced once electrical conductivity exceeds 4,500 µS cm^{-1}, where the Cl^-–EC correlation reaches 0.87 (Fig 14a). By contrast, groundwater from the Albian aquifer shows much steadier and more balanced chloride and sulfate levels (Fig 14b). The consistently high chloride concentrations are the primary factor responsible for the elevated mineralization observed in these waters.

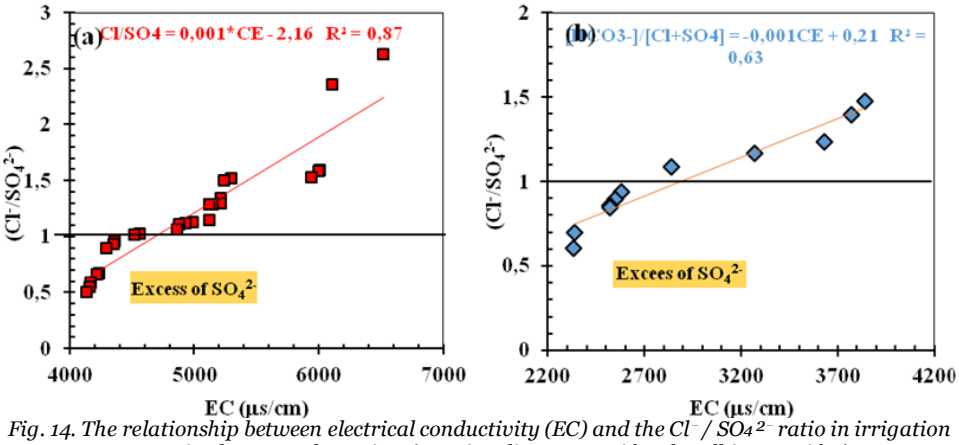


Fig. 14. The relationship between electrical conductivity (EC) and the Cl^- / SO_4^{2-} ratio in irrigation waters in the Ouargla region (a: Mio-Pliocene aquifer; b: Albian aquifer)

3.2.4. Base exchange processes

Throughout their underground flow, groundwater gradually becomes charged with dissolved matter, where it encounters elements capable of initiating ionic exchange with water. This is a distinctive characteristic of clays; whose layers carry a negative charge. This charge is compensated in the interlayer spaces by exchangeable cations such as Na^+, H^+, K^+, Mg^{2+}, and Ca^{2+} (Al-Droubi, 1976; Feumba et al., 2021).

3.2.5 Base Exchange Index (BEI)

The use of this index allows us to determine the exchanges in clay minerals, the exchanges that occur between the liquid phase and the solid phases during the underground flow of water. Indeed, clay minerals perform ion exchanges, where Na^+ and K^+ ions in solution are exchanged for Ca^{2+} and Mg^{2+} ions. The Base Exchange index (BEI) is defined as the ratio of exchanged ions to the ions of the same nature that were initially present in the water. It is calculated using the following formula (Al-Droubi, 1976; Feumba et al., 2021):

$$BEI = \frac{[Cl^- - Na^+ - K^+]}{Cl^-}, \quad (2)$$

where The Base Exchange Index (BEI) offers insight into cation exchange processes between groundwater and surrounding soil. When BEI < 0, it indicates that cation exchange is occurring through the introduction of Ca^{2+} and Mg^{2+} into the water, as these ions replace Na^+ and K^+ from the soil due to contact with clay minerals. Conversely, when BEI > 0, the water undergoes a reverse exchange, where Na^+ and K^+ are consumed-typically by vegetation through evapotranspiration and chloride re-concentration-leading to their replacement by Ca^{2+} and Mg^{2+} from the soil. A BEI value of zero

(BEI = 0) reflects a chemical equilibrium between the groundwater and the surrounding geological medium.

The projection of the BEI values in fig 15a and fig 15b, indicates that there are six wells of Mio-Pliocene aquifer (F1; F4; F5; F6; F11 and F14) and four wells of the Albian aquifer (F29; F32; F33 and F36), presenting negative BEIs. There is a positives values of the BEI in more than 81% of the samples for the Mio-Pliocene and more than 63% of samples for the Albian. Fig 15 depicts the evolution of the Base Exchange Index (BEI) in the irrigation waters of the Ouargla region in Mio-Pliocene aquifer and Albian aquifer.

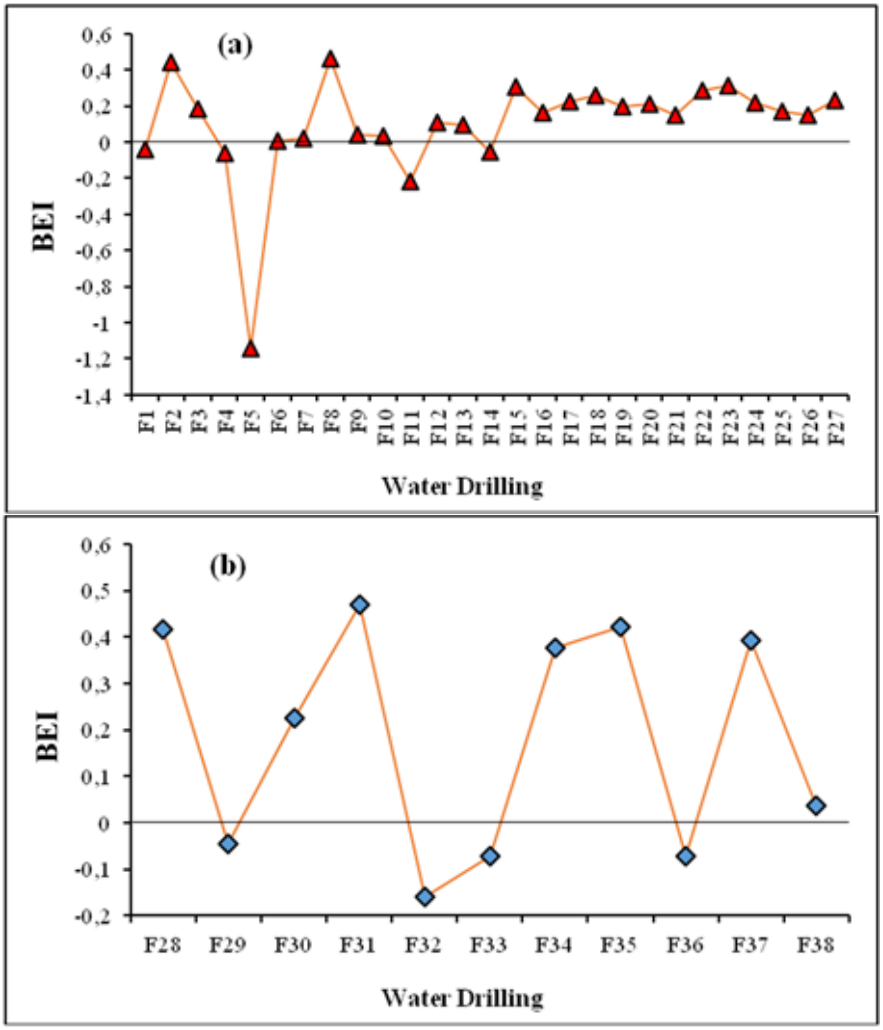


Fig. 15. Evolution of the Base Exchange Index (BEI) in the irrigation waters of the Ouargla region, a: Mio-Pliocene aquifer; b: Albian aquifer

The major geochemical phenomena occur within the aquifer, involving mechanisms related to carbonate chemistry and base exchange. It was previously observed, with regard to calcium, that the relationship between the sum of alkaline earth cations

(in meq/L) and bicarbonate ions is characterized by a weak correlation. The reason for this was the input of dissolving gypsum, along with saturation in dolomite and calcite. However, it is important to take into consideration the significant contribution of trapped waters in sedimentary deposits to properly explain the evolution of chemical facies, and to account for base exchanges and/or possible cation inputs resulting from silicate hydrolysis. Fig 16 highlights the fundamental ion exchange processes through the relationship between [Ca^{2+}+ Mg^{2+}– HCO_3^-– SO_4^{2-}] and [Na^++ K^+– Cl^-] in the waters of the Mio-Pliocene and Albian aquifers.

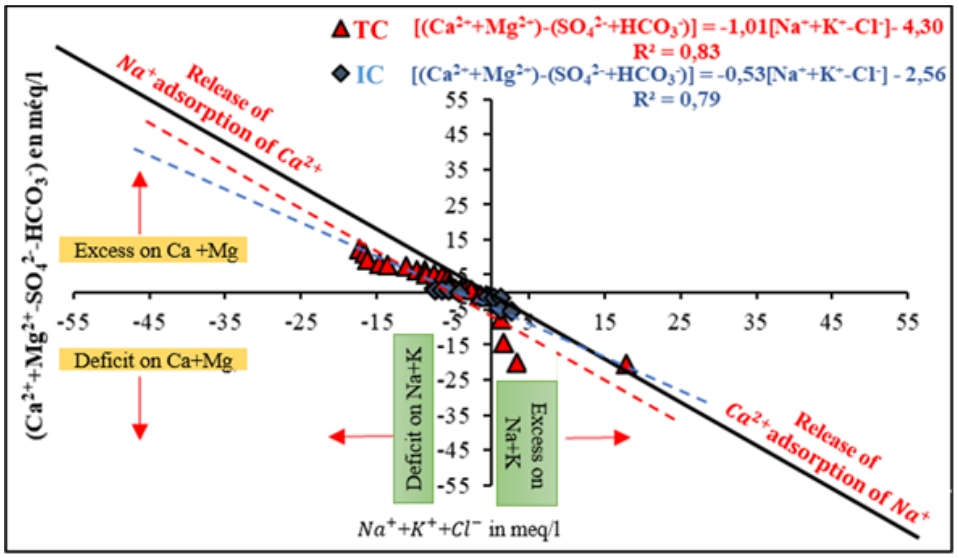


Fig. 16. Highlighting fundamental exchange processes through the relationship between [Ca^{2+} + Mg^{2+}– HCO_3^- – SO_4^{2-}] and [Na^+ + K^+– Cl^-] in the waters of the Mio-Pliocene and the Albian

The [Ca^{2+} + Mg^{2+} – HCO_3^- – SO_4^{2-}] versus [Na^+ + K^+ – Cl^-] diagram in fig 16 exhibits strong linear trends, with coefficients of determination of R^2 = 0.83 for the Mio-Pliocene aquifer and R^2 = 0.79 for the Albian aquifer, indicating that cation-exchange processes are well developed in both systems. Samples plotting far from the origin highlight the key role of Na^+ and Ca^{2+} in ion exchange between groundwater and clay minerals during aquifer residence. Overall, the diagram confirms an active exchange mechanism in which clays release Na^+ and/or K^+ while adsorbing Ca^{2+} and/or Mg^{2+}- and occasionally the reverse-thereby governing the hydrochemical evolution of these waters.

3.2.6. Water–sediment interaction.

The analysis of the saturation index (SI) values for key minerals, illustrated in Fig 17, indicates that groundwater from both aquifers is under saturated with respect to gypsum and anhydrite, suggesting active dissolution of these evaporate minerals where calcium (Ca^{2+}) and sulfate (SO_4^{2-}) concentrations are elevated. Similarly, the observed under saturation with respect to halite confirms the significant contribution of rock salt dissolution to the salinity of irrigation waters. This is further supported by the high levels of sodium and chloride, which reflect prolonged water–rock interaction and extended subsurface residence times. Fig 17 illustrates the saturation Index with Respect to the Main Minerals (Carbonates/Sulfates).

For dolomite, 14% of the water samples from the Mio-Pliocene aquifer and only one sample from the Albian aquifer (Sample No. 29) exhibit a saturation index below zero, indicating under saturation with respect to dolomite. The remaining samples-86% from the Mio-Pliocene and 99% from the Albian-are supersaturated. Similar trends were observed for calcite. The precipitation of these minerals generally occurs in the northern part of the Mio-Pliocene aquifer, contributing to a balance in Ca^{2+} concentrations. Regarding aragonite, 26% of the Mio-Pliocene samples are under saturated, while this percentage increases to 45% in the Albian samples, indicating a greater tendency for aragonite precipitation in the latter.

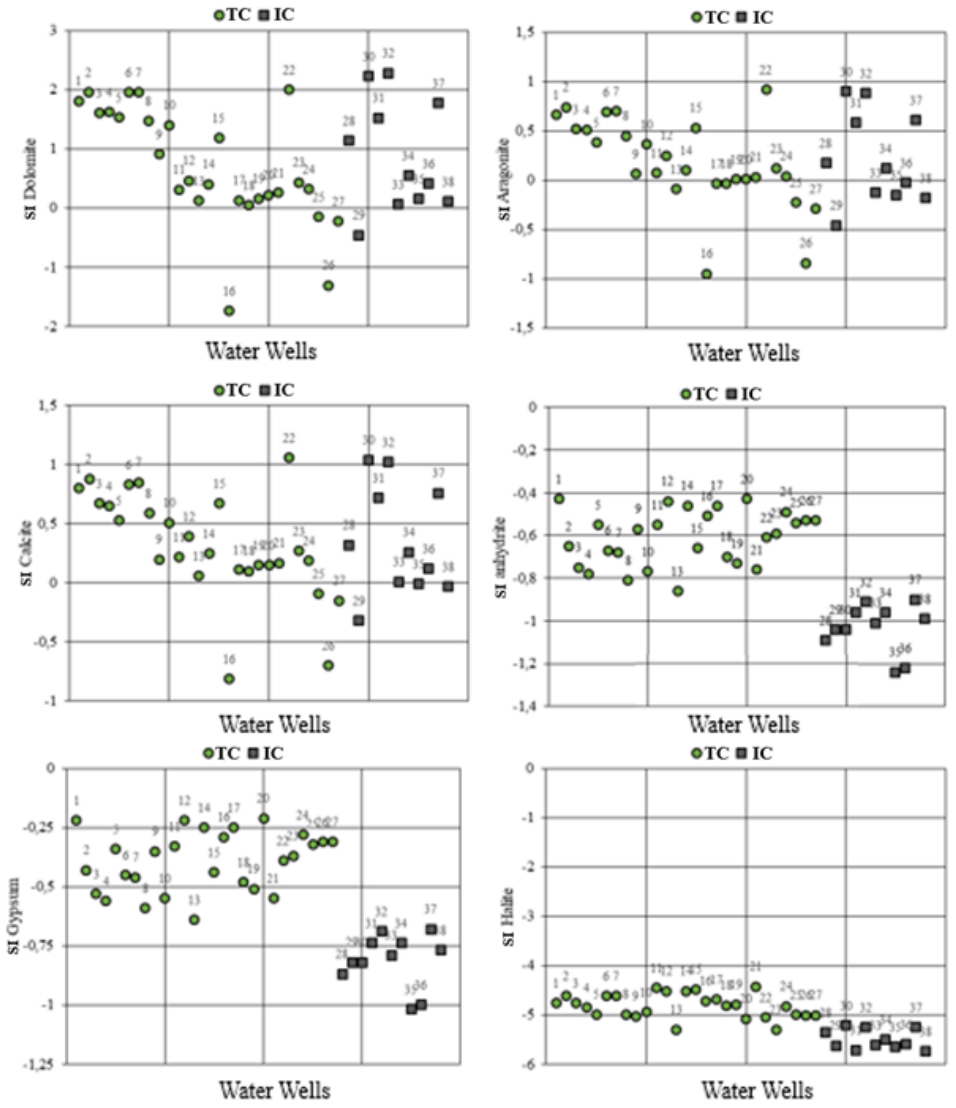


Fig. 17. Saturation Index with Respect to the Main Minerals (Carbonates/Sulfates)

3.2.7. Concentration diagram

The concentration diagram in fig 18 shows that chloride values align closely along a straight line with a slope of 1 when plotting the logarithm of concentration factor against the logarithm of ionic concentrations (meq/L). This indicates that chloride concentrations increase proportionally with water concentration, confirming its role as a reliable tracer of salinity. Other elements deviate from this pattern, reflecting differences in their behavior during the concentration process, with some increasing and others decreasing relative to chloride. Fig 18 illustrates the evolution of major element concentrations as a function of the concentration factor in the irrigation water of the Mio-Pliocene aquifer.

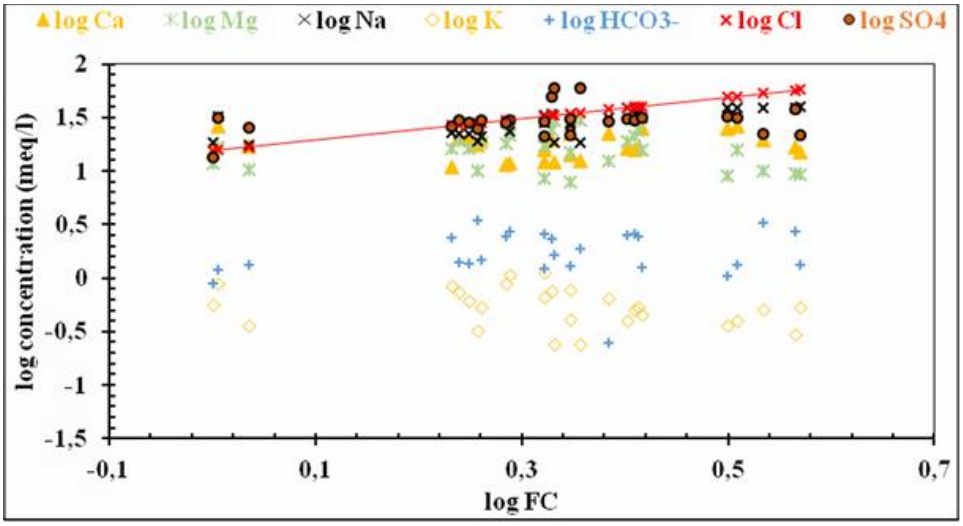


Fig. 18. Evolution of major element concentrations as a function of the concentration factor in the irrigation water of the Mio-Pliocene aquifer

According the Fig 18 the alkalinity (alc - 2Ca - 2Mg < 0) in the initial solution is lower than the sum of the equivalent concentrations of magnesium and calcium. The rate of increase in Ca and Mg concentrations is less than that of the concentration factor, which is consistent with the negative residual alkalinity due to calcite (alc - 2Ca < 0). The scatter plot of these concentration values curves downward, indicating a consumption of magnesium and calcium, while sulfate concentrations remain high, corresponding to a positive residual alkalinity due to calcite plus gypsum (alc - 2Ca + $2SO_4$ > 0) and a positive residual alkalinity due to gypsum ($2SO_4$ - 2Ca - 2Mg > 0).

3.2.8. Salt/solution equilibrium and ion behavior

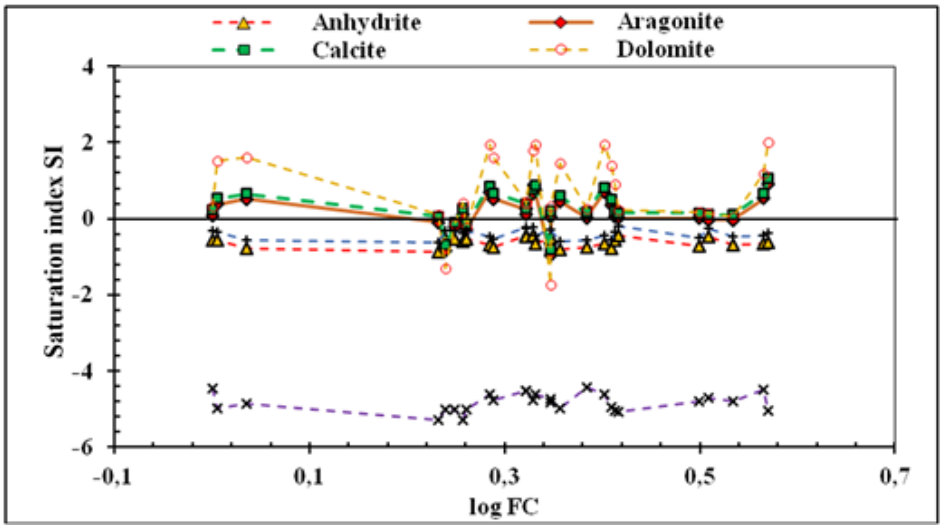


Fig. 19. Evolution of the mineral saturation index in Mio-Pliocene water as a function of the concentration factor

Fig 19 presents the saturation index (SI) of minerals on the y-axis versus the logarithm of the concentration factor (log Fc) on the x-axis in Mio-Pliocene water. It is observed that from the onset of concentration (log Fc < 0.2), the waters are already at or beyond equilibrium, indicating saturation or supersaturation. This condition favors the precipitation of minerals such as dolomite ($CaMg(CO_3)_2$), calcite ($CaCO_3$), and aragonite ($CaCO_3$), which play a key role in regulating alkalinity (as bicarbonate) and controlling calcium and magnesium concentrations, preventing their simultaneous increase.

4. Conclusion

The comprehensive hydrogeochemical analysis of the Mio-Pliocene (TC) and Albian (IC) aquifers in the Ouargla region reveals a complex interplay of natural processes that govern groundwater quality and its suitability for irrigation. The region's hyper-arid climate, characterized by extremely low precipitation and high evapotranspiration, creates a significant water deficit, making groundwater resources critically important.

Our findings highlight that evaporate dissolution is the dominant hydrochemical process influencing both aquifers. This is evident from the prevalence of high concentrations of major ions such as Cl^- and SO_4^{2-}, as well as Na^+ and Ca^{2+}. The Chadha diagram analysis further supports this, showing distinct hydrochemical facies. The Mio-Pliocene aquifer primarily exhibits Ca-Mg-SO_4 or Ca-Mg-Cl water types, along with a significant Na-Cl type, while the Albian aquifer is overwhelmingly dominated by the Ca-Mg-SO_4 or Ca-Mg-Cl facies.

Cation exchange processes also play a crucial role in shaping the groundwater chemistry, particularly influencing sodium and calcium concentrations. The consistently high Na^+ and K^+ contents, alongside Cl^- dominance, suggest halite and potassium chloride dissolution. However, the observed excess of sodium over calcium in many samples, further supported by the ($[Na^+/Cl^-]$) vs. ($[Ca^{2+}/(HCO_3^- + SO_4^{2-})]$) diagram, points to active ion exchange where Na+

from clay minerals replaces Ca^{2+} in the groundwater. This process is more pronounced in the Mio-Pliocene aquifer, likely due to the presence of carbonate formations and silty clays. The Base Exchange Index (BEI) values further confirm these exchange reactions, with a majority of samples showing positive BEI, indicating Na^{+} and K^{+} consumption and replacement by Ca^{2+} and Mg^{2+} from the soil.

The saturation indices confirm the under saturation of groundwater with respect to gypsum, anhydrite, and halite, driving their dissolution and contributing to the elevated salinity. Conversely, a high percentage of samples show supersaturation with respect to dolomite and calcite, especially in the Mio-Pliocene aquifer, suggesting the precipitation of these minerals and a regulatory effect on Ca^{2+} concentrations. The relationship between electrical conductivity (EC) and the carbonate/evaporite ratio further underscores the impact of evaporite dissolution on overall water mineralization.

The groundwater in the Ouargla region's Mio-Pliocene and Albian aquifers is primarily characterized by the dissolution of evaporitic minerals, leading to high salinity. This natural mineralization is further modified by active cation exchange with clay minerals, which significantly affects the balance of major cations. Understanding these hydrogeochemical processes is critical for sustainable management of these vital groundwater resources in a water-scarce environment like Ouargla.

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Conflict of Interest: The authors declare no conflict of interest.

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