



## Hydrogeological and Hydrogeochemical Insights into Groundwater Mineralization: A Spatiotemporal Analysis of the Terminal Complex Aquifer in Wadi Righ, Southern Algeria

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### ABSTRACT

Groundwater in the Algerian Sahara is an important source of water for various uses. Despite its abundance compared to surface water, it is still confronted to many problems, in terms of overexploitation and quality. Excessive mineralization of this groundwater is a major issue in the Wadi Righ region in northeastern Algerian Sahara. In this paper, we attempt to examine the groundwater mineralization source of the Terminal Complex aquifer and analyze its spatiotemporal trends by combining tools from Geographic Information Systems (GIS) with hydrogeochemical analysis of results from 117 wells between a period of four years (1995, 2012, 2015 and 2017), and 613 groundwater measurements for six years (1998, 2005, 2010, 2013, 2015 and 2017). The groundwater exhibits electrical conductivity values ranging from 2760 to 11200  $\mu\text{S}/\text{cm}$  and TDS concentrations between 1934 and 8318 mg/L, indicating strong mineralization gradients from south to north. The dominant hydrochemical facies are  $\text{SO}_4\text{-Cl-Mg-Ca}$  and  $\text{SO}_4\text{-Cl-Na}$ . Hydrogeochemical diagrams reveal that water-rock interaction and evaporite dissolution are the main processes controlling salinity. Spatial mapping of EC, groundwater levels, and saturation indices (SI) indicates a progressive increase in salinity toward Chott Merouane, with an inverse correlation between groundwater level and mineralization. This study provides the first integrated spatiotemporal assessment combining hydrogeochemical and GIS-based approaches to characterize the evolution of groundwater salinity in the Wadi Righ basin, contributing new insight into the link between aquifer depletion and mineralization in the Algerian Sahara.

*Keywords* Groundwater; Wadi Righ; Terminal Complex; Mineralization; Spatiotemporal trends.

## Perspectivas hidrogeológicas e hidrogeoquímicas sobre la mineralización de aguas subterráneas: Un análisis espaciotemporal del acuífero Complejo Terminal en Wadi Righ, sur de Argelia

### RESUMEN

Las aguas subterráneas en el Sahara argelino constituyen una fuente importante de agua para diversos usos. A pesar de su abundancia en comparación con las aguas superficiales, enfrentan numerosos problemas relacionados con la sobreexplotación y la calidad. La mineralización excesiva de estas aguas es un problema grave en la región de Wadi Righ, en el noreste del Sahara argelino. En este artículo, se busca examinar la fuente de mineralización de las aguas subterráneas del acuífero Complejo Terminal y analizar sus tendencias espaciotemporales, combinando herramientas de Sistemas de Información Geográfica (SIG) con el análisis hidrogeoquímico de los resultados de 117 pozos durante un período de cuatro años (1995, 2012, 2015 y 2017), y 613 mediciones de aguas subterráneas durante seis años (1998, 2005, 2010, 2013, 2015 y 2017). Las aguas subterráneas presentan valores de conductividad eléctrica que varían entre 2760 y 11200  $\mu\text{S}/\text{cm}$  y concentraciones de sólidos disueltos totales (TDS) entre 1934 y 8318 mg/L, lo que indica fuertes gradientes de mineralización de sur a norte. Los facies hidroquímicos dominantes son  $\text{SO}_4\text{-Cl-Mg-Ca}$  y  $\text{SO}_4\text{-Cl-Na}$ . Los diagramas hidrogeoquímicos revelan que la interacción agua-roca y la disolución de evaporitas son los principales procesos que controlan la salinidad. La cartografía espacial de la CE, los niveles de agua subterránea y los índices de saturación (IS) indica un aumento progresivo de la salinidad hacia Chott Merouane, con una correlación inversa entre el nivel freático y la mineralización. Este estudio presenta la primera evaluación espaciotemporal integrada que combina enfoques hidrogeoquímicos y basados en SIG para caracterizar la evolución de la salinidad de las aguas subterráneas en la cuenca de Wadi Righ, aportando nuevos conocimientos sobre la relación entre el agotamiento del acuífero y la mineralización en el Sahara argelino.

*Palabras clave:* aguas subterráneas; Wadi Righ; Complejo Terminal; mineralización; tendencias espaciotemporales.

### Record

Manuscript received: 08/02/2024

Accepted for publication: 02/01/2026

### How to cite this item:

Bettahar, A., Eddine Nezli, I., Sener, S., Kechiched, R., Ajiboye, J. O., & Sener, E. (2025). Hydrogeological and Hydrogeochemical Insights into Groundwater Mineralization: A Spatiotemporal Analysis of the Terminal Complex Aquifer in Wadi Righ, Southern Algeria. *Earth Sciences Research Journal*, 29(4), 441-457. <https://doi.org/10.15446/esrj.v29n4.112389>

## 1. Introduction

Groundwater in arid and semi-arid regions represents a critical resource, providing the main supply for domestic, agricultural, and industrial uses. Although it accounts for only about 30% of global freshwater, groundwater remains the most reliable source in water-scarce regions (Çelik and Yildirim, 2006; Gallardo and Tase, 2007; Partey et al., 2010; Hosseini and Mirzaei, 2015; Mirzavand & Ghazavi, 2015; Carreira et al., 2018; Carrard et al., 2019).

In the Algerian Sahara, the scarcity and poor quality of surface water have led to increasing dependence on groundwater, often without considering the risks of overexploitation and salinization. Salinization and mineralization are major threats to groundwater quality worldwide (Polemio et al., 2009; Edmunds, 2012; Bahir et al., 2018; Foster et al., 2018; Lyazidi et al., 2019; Thorslund and van Vliet, 2020; Arani et al., 2023; Ashik and Gain, 2023; Drouiche et al., 2011, 2024).

Hydrogeochemical research is a highly relevant field in the Mediterranean region due to the increasing challenges in water security (Voutsis et al., 2015; Mongelli et al., 2019). The use of hydrogeochemical techniques to understand geochemistry and water quality has piqued the interest of researchers from around the world (De Montety et al., 2008; Prasanna et al., 2010; Gaofeng et al., 2010; Zhu and Schwartz, 2011; Alexakis, 2011; Ryzhenko and Cherkasova, 2012; Ahmed et al., 2013; Voutsis et al., 2015; Zhang et al., 2015; Nair et al., 2015; Nematahli et al., 2016; Walter et al., 2017; Barzegar et al., 2017; Sánchez et al., 2017; Madhav et al., 2018; Wang et al., 2022; Dhaoui et al., 2023; Khezami et al., 2024).

In arid and semi-arid settings, these processes are largely driven by evaporite dissolution, evaporation, and limited recharge (Galego Fernandes et al., 2005; Singhal et al., 2020; Lal et al., 2023; Vetrimurugan et al., 2023; Alqarawy, 2023; Vespasiano et al., 2023), but can also be aggravated by anthropogenic pressures, including agricultural and industrial activities (Drouiche et al., 2013; Aghazadeh et al., 2017; M'nassri et al., 2019). Understanding these processes is essential for effective groundwater management.

The use of hydrogeochemical techniques to understand geochemistry and water quality has piqued the interest of researchers from around the world (De Montety et al., 2008; Prasanna et al., 2010; Gaofeng et al., 2010; Zhu and Schwartz, 2011; Alexakis, 2011; Ryzhenko and Cherkasova, 2012; Ahmed et al., 2013; Voutsis et al., 2015; Zhang et al., 2015; Nair et al., 2015; Nematahli et al., 2016; Walter et al., 2017; Barzegar et al., 2017; Sánchez et al., 2017; Madhav et al., 2018; Wang et al., 2022; Dhaoui et al., 2023; Zahi et al., 2024). Previous hydrogeochemical studies in the Terminal Complex aquifer of the northern Sahara, including the Wadi Righ basin, have described the geochemical composition and sources of salinity (Edmunds et al., 1997; Guendouz et al., 2003; Voutsis et al., 2015; Bettahar et al., 2017a,b; Mongelli et al., 2019; Houari et al., 2019; Ouarekh et al., 2021; Hammadi et al., 2022; Bettahar and Şener, 2022).

The groundwater chemistry of the Terminal Complex aquifer in the northern Sahara, in general, and in the Wadi Righ area, in particular, has been extensively studied by many researchers (Edmunds et al., 1997; Guendouz et al., 2003; Belksier et al., 2016; Bettahar et al., 2017b; Houari et al., 2019; Ouarekh et al., 2021; Reghais et al., 2023, 2024; Bettahar et al., 2025). In a study conducted by (Bettahar et al., 2017a), they used various statistical methods and concluded that the geochemical origin of water mineralization in the Terminal Complex has a geological basis. Meanwhile, Houari et al. (2019) found that the water in the Wadi Righ region has high levels of mineralization due to the solubility of mineral salts in the soil and rocks. The results obtained by Bettahar et al. (2017b) indicated that the presence of high levels of dissolved ions results from the water's contact with geological formations. However, most of these works have focused on single-year assessments or general descriptions of hydrochemical facies, with limited attention to the spatiotemporal evolution of mineralization over time.

This study aims to fill that gap by examining the origin and spatial-temporal variability of groundwater mineralization in the Terminal Complex aquifer of Wadi Righ. We combine hydrogeochemical data from more than 700 samples collected over two decades with GIS-based spatial analysis to (1) identify the main processes controlling mineralization, (2) assess its temporal evolution, and (3) explore the relationship between mineralization and groundwater level. The novelty of this study lies in its integration of long-term multi-year hydrochemical data and spatial modeling, offering the first comprehensive assessment of mineralization trends in this Saharan aquifer.

The results contribute to improving regional groundwater management and understanding of hydrogeochemical processes in arid environments. Nevertheless, interpretation remains limited by the spatial distribution of sampling wells and the availability of continuous time-series data.

## 2. Materials and Methods

### Study area

Geographically, the Wadi Righ region is located in the northeast of the Algerian desert (Fig. 1). It is situated between latitudes from 32° 54' to 39° 9' N and longitudes from 5° 50' to 5° 75' E. The altitude changes from 145 m at El Goug upstream to less than 35 m at Chott Merouane. The total area of the valley exceeds 3,000 km<sup>2</sup>, with an overall slope of approximately 1% from south to north.

As reported by Bettahar and Şener (2022), the Wadi Righ region has a dry climate with moderate winters. It is characterized by a high monthly evaporation rate, with its peak in July at 399.79 mm and a low evaporation rate in December at 107.39 mm. It also has low and inconsistent annual precipitation, averaging around 74.84 mm (Habes et al., 2016). According to Bettahar et al. (2017b), the average annual temperature in this area is around 21.96 °C.

The geological formations of the studied area have been described by many authors (Paix, 1956; Cornet, 1964; Bel and Demargne, 1966; Bel and Cuhe, 1970; Bel et al., 1970; UNESCO, 1972; Faber et al., 1976; Guendouz et al., 2003; Melouah and Pham, 2021).

From the oldest to the most recent (Fig. 2), the following geological formations may be distinguished (Cornet, 1964; Faber et al., 1976):

- The Albian is presented as a very thick (# 450 m) series composed of an alternation of sandy layers with passages of shale clay.
- The Vraconian consists in an irregular alternation of clay and dolomitic levels, sandy clays and more rarely passages of sandstone with limestone cement.
- The Cenomanian has a considerable thickness that gradually decreases towards the north. It outcrops in the atlasic zone. It is composed essentially of marly lagoonal deposits where layers of anhydrite and sometimes even salt predominate.
- The Turonian is represented by a marine, calcareous-marly deposit, and its thickness remains fairly constant.
- The Senonian is essentially made up of white limestone with an alternation of marly limestone and layers of gypsum. It is formed of two very different sets from a lithological point of view: the lagoonal Senonian, at the base, and the carbonate Senonian, above.
- The Eocene is composed of two distinct lithologic sets: a lower carbonate set and an upper evaporite set. The lower Eocene carbonate level has characteristics that make it difficult to distinguish from the Senonian. The presence or absence of nummulites is the main difference. Limestones are generally more frequent than dolomites and evaporites are much rarer or completely absent compared to the Senonian. The flint limestones encountered at the top of the Senonian carbonate continue into the Eocene. The thickness of this formation varies between 100 and 500 meters. The middle level of the Eocene evaporite is composed of an alternation of limestone, anhydrite and marls, and its thickness reaches about 100 meters under the Chotts (Bel and Cuhe, 1969). In the Wadi Righ, the limestone formation seems to be located in a carbonate level belonging to the Eocene evaporite.
- The lenticular deposits of the Mio-pliocene are divided into four levels according to Bel and Demargne (1966). Level 1 is composed of thin clay layers, found only in the central zone of the Eastern Sahara, forming a poorly permeable barrier between the Senonian and Eocene carbonate aquifers and the sands of level 2. Level 2 is a thick and consistent gravelly-sandy layer, sometimes containing gravel at the base and clay at the top, reaching 400 meters in thickness in the South of Gassi Touil. It is the main aquifer horizon of the Mio-Pliocene. Level 03 is a poorly defined clay-sandy formation, impermeable and present only in certain areas, particularly in the region of the chotts. Level 04 is a sandy layer, sometimes continuing from level 02, containing a crust of gravel-limestone at the top and 300 meters in thickness.
- The Quaternary deposits are mainly sandy, located beneath semi-permeable clay and evaporite layers. These Quaternary formations are the source of the phreatic aquifer, which is mainly fed by the infiltration of water from wadis and especially by the percolation of excess water during irrigation periods.

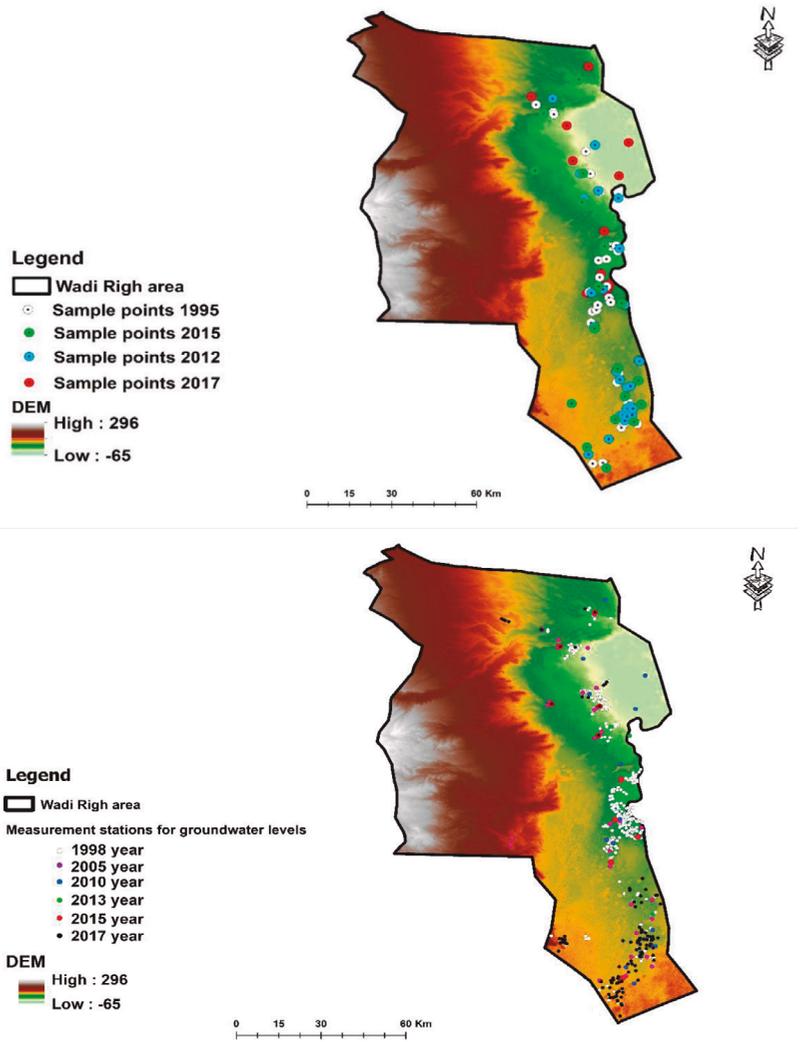


Figure 1. Measurement stations of groundwater samples in Wadi Righ

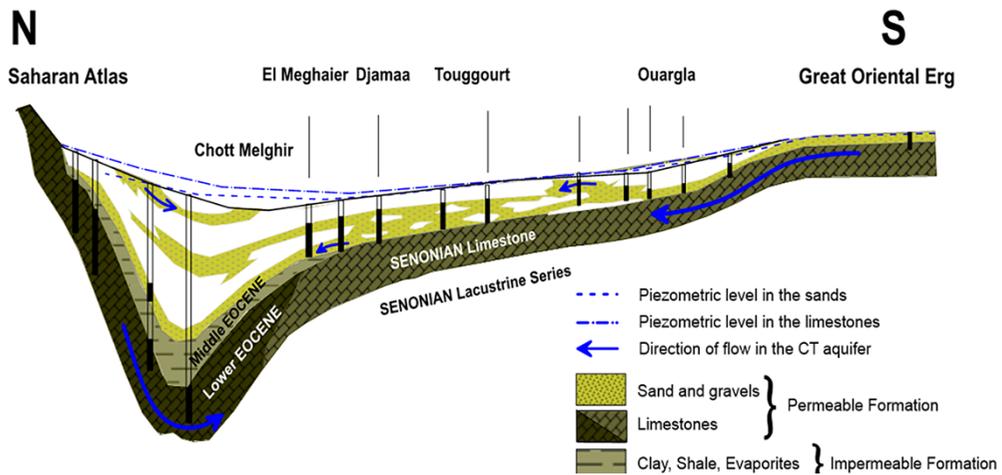


Figure 2. Hydrogeological cross section of the Terminal Complex aquifer of the northern Sahara in Algeria (after Guendouz et al. 2003, Bettahar et al. 2025)

### Sampling and hydrogeochemical methods

In the valley of Wadi Righ, the aquifer of the Terminal Complex underwent sampling by the Algerian Water (ADE) and the National Agency for Water Resources (ANRH) in 1995, 2012, 2015, and 2017. A total of 117 wells were included in these sampling efforts. The collected samples were analysed at the ADE and ANRH laboratories, following standard techniques. The measurements and analysis involved the use of various instruments and methodologies. Nitrates, Sulphates, and Chlorides were quantified using the HACH DR2000 spectrophotometer. Flame spectrophotometry (Coming 410) was utilized to analyze Calcium, Sodium, and Potassium levels. Magnesium levels were determined through complexometric titration using ethylenediaminetetraacetic acid (EDTA) as the titrant, with the equation  $Mg^{2+} = TH - Ca^{2+}$ . Bicarbonates were measured using a pH meter Type E632 (METLOOHM), while pH and electrical conductivity (EC) were measured in situ. Total dissolved solids (TDS) were measured directly in the laboratory by gravimetric determination. To map the distribution of groundwater levels, 613 groundwater samples distributed over 6 years (1998, 2005, 2010, 2013, 2015, and 2017) were used, to ensure an even distribution and a significant periodical coverage to facilitates a clearer, accurate or more precise results.

In this study, the analytical data were tested and validated by the Aq.QA program, Demo 1.1 version (RockWare, Inc., Golden, Colorado, USA). The relationship between the major ions were investigated using bivariate plots and Chadha diagrams. The PIPER diagram was established using the DIAGRAMMES v2.00 software for classified groundwater facies, and the saturation indices were calculated using the PHREEQC Interactive v3.7.3 software to assess the influence of water/rock interaction on the composition of groundwater in the Wadi Righ region, and we used ArcGIS 10.3 and its spatial analyst tool (Inverse Distance Weighting Interpolation) to map the

spatial distribution of electrical conductivity (EC), total dissolved solids (TDS), saturation indices (SI) of groundwater, and water level in the study area (Fig. 3).

### 3. Results and Discussion

#### Hydrogeochemical facies and water type

#### Piper diagram

Most water samples from the Terminal Complex aquifer (1995-2012-2015-2017) are traced in zone 4 (Fig. 4), indicating that strong acids ( $SO_4 + Cl$ ) exceed weak acids ( $HCO_3$ ), and for most water samples, the alkaline earth (Ca + Mg) exceed the alkalis (Na + K). The plotted points of water samples in zone 6 indicates that non-carbonate hardness exceeds 50%, while other water samples in zone 7 indicates that non-carbonate alkali hardness exceeds 50%. After the classification to different cations and anions the dominant facies are calcium, magnesium, chloride and sulfate for most waters and sodium chloride and sulfate facies for the other samples of the Terminal Complex aquifer in the Wadi Righ region.

#### Chadha diagram

The Chadha diagram (Fig. 5) was used to understand the main geochemical processes behind the groundwater chemistry in the study area (Chadha, 1999; Fu et al., 2018; Yang et al., 2019). This diagram provides a clearer representation of the evolution of hydrochemical processes. To determine the primary water type, the rectangular area of the diagram is divided into eight sub-regions, each characterizing a specific hydrogeochemical water type:

Region 1: Alkaline earth elements exceed alkali elements.

Region 2: Alkali elements exceed alkaline earth elements.

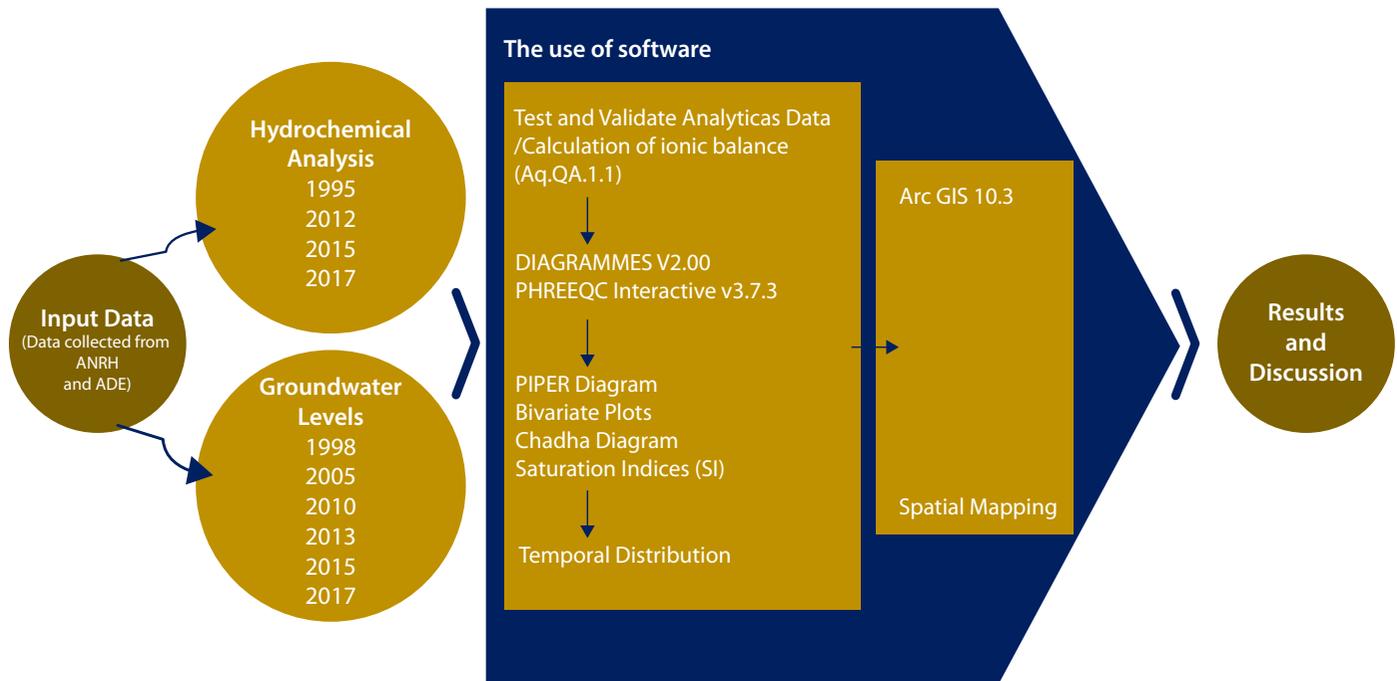


Figure 3. Flowchart of the study

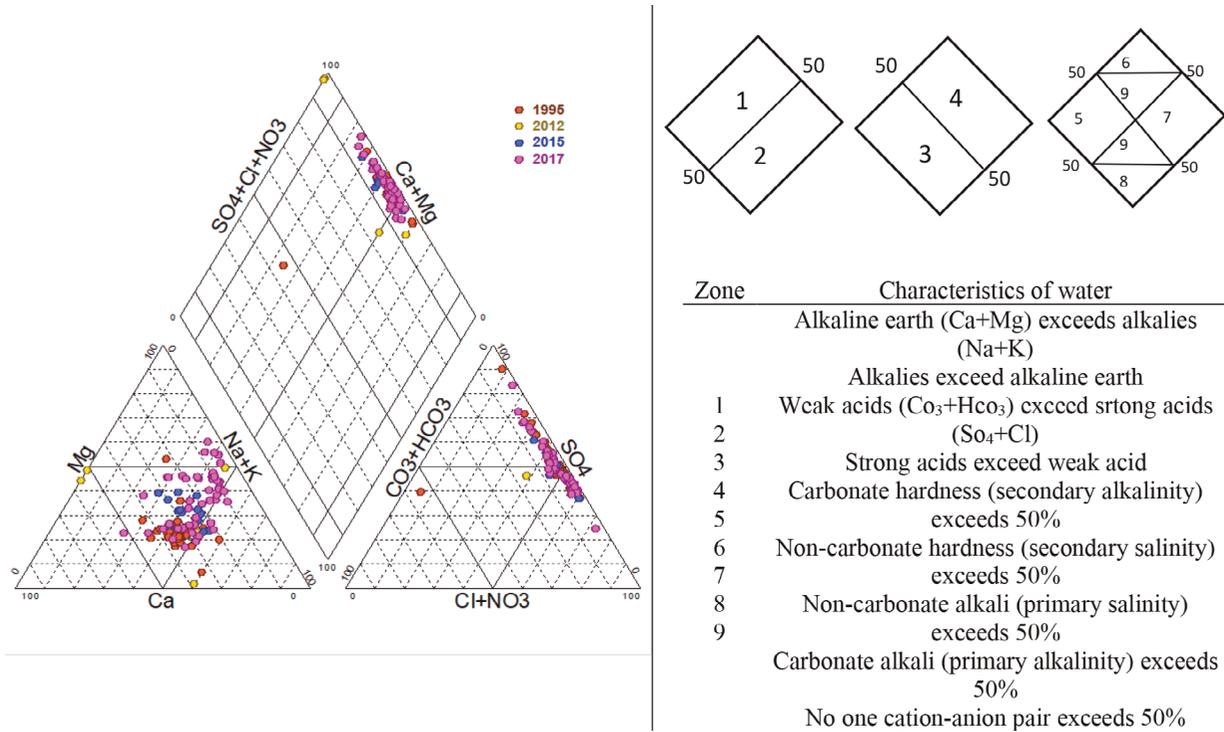


Figure 4. Piper diagram of Terminal Complex groundwater samples (1995-2012-2015 and 2017)

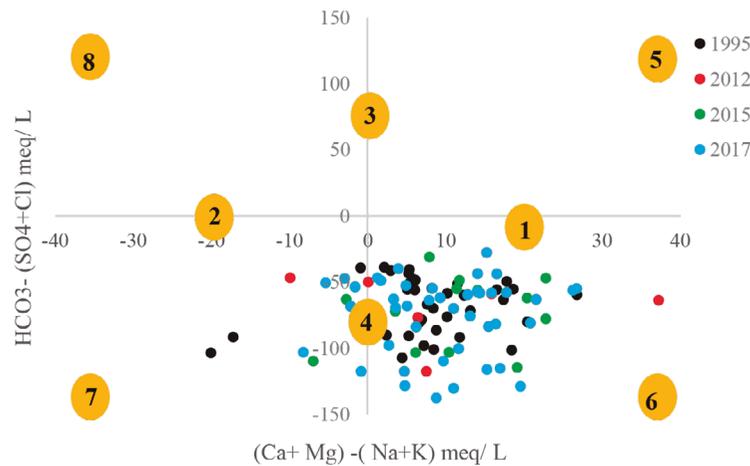


Figure 5. Chadha diagram for the groundwater classification in the Terminal Complex aquifer (1995, 2012, 2015 and 2017)

Region 3: Weak acidic anions exceed strong acidic anions.

Region 4: Strong acidic anions exceed weak acidic anions.

Region 5: Alkaline earth elements and weak acidic anions exceed alkali metals and strong acidic anions, respectively. This type of water exhibits temporary hardness. The data points in this region of the diagram represent Ca<sup>2+</sup>-Mg<sup>2+</sup>-HCO<sub>3</sub><sup>-</sup> type, Ca<sup>2+</sup>-Mg<sup>2+</sup> dominant HCO<sub>3</sub><sup>-</sup> type, or HCO<sub>3</sub><sup>-</sup> dominant Ca<sup>2+</sup>-Mg<sup>2+</sup> type waters.

Region 6: Alkaline earth elements exceed alkali metals, and strong acidic anions exceed weak acidic anions. This type of water exhibits permanent hardness and does not accumulate residual sodium carbonate when used for irrigation. The data points in this region represent Ca<sup>2+</sup>-Mg<sup>2+</sup>-Cl<sup>-</sup> type, Ca<sup>2+</sup>-Mg<sup>2+</sup> dominant Cl<sup>-</sup> type, or Cl<sup>-</sup> dominant Ca<sup>2+</sup>-Mg<sup>2+</sup> type waters.

Region 7: Alkali metals exceed alkaline earth elements, and strong acidic anions exceed weak acidic anions. This type of water generally causes salinity

issues in irrigation and drinking water usage. The data points in this region represent Na<sup>+</sup>-Cl<sup>-</sup> type, Na<sub>2</sub>SO<sub>4</sub> type, Na<sup>+</sup> dominant Cl<sup>-</sup> type, or Cl<sup>-</sup> dominant Na<sup>+</sup> type waters.

Region 8: Alkali metals exceed alkaline earth elements, and weak acidic anions exceed strong acidic anions. This type of water accumulates residual sodium carbonate when used for irrigation and causes foaming issues. The data points in this region represent Na<sup>+</sup>-HCO<sub>3</sub><sup>-</sup> type, Na<sup>+</sup> dominant HCO<sub>3</sub><sup>-</sup> type, or HCO<sub>3</sub><sup>-</sup> dominant Na<sup>+</sup> type waters (Chadha, 1999).

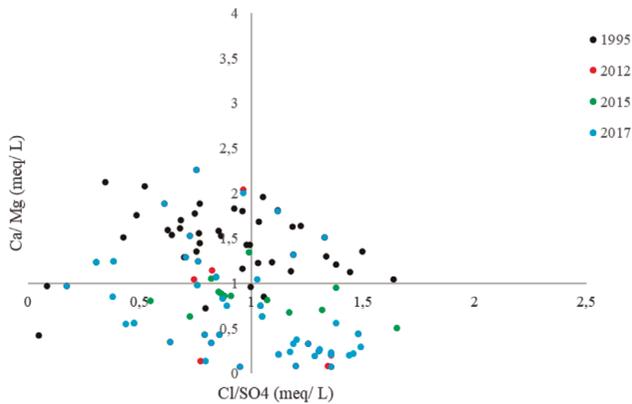
According to the Piper diagram classification (Fig. 4), the found facies is Ca-Mg-Cl-SO<sub>4</sub> for most of the samples and this type could be explained by ion exchange mechanisms between groundwater and geological strata (Ouarani et al., 2020). This is indicated by the Chadha diagram which confirms the dominance of the Ca-Mg-Cl-SO<sub>4</sub> type for most of the water samples from the four sampling campaigns.

### Hydrogeochemical processes controlling groundwater mineralization

#### Origin of groundwater mineralization

##### Ca/Mg vs. Cl/SO<sub>4</sub>

According to Figure 6, when the SO<sub>4</sub>/Cl ratio shows values greater than 1, it indicates an enrichment in chloride ions. If the ratio is less than 1, it indicates an enrichment in sulfate ions. The Ca/Mg ratio, showing values greater than 1, indicates an enrichment in calcium, while value less than 1, indicates an enrichment in magnesium. The dominant facies found in 1995 is the calcium chloride and sulfate (31 samples out of 33). Most of the observations had the magnesium chloride and sulfate facies in the years 2012, 2015, and 2017, while calcium and magnesium chloride for other water samples. The variations of the chemical facies probably reflects the heterogeneous geological formations containing the Terminal Complex aquifer (Guendouz et al., 2003; Bettahar et al., 2017b; Houari et al., 2019).



**Figure 6.** Relationships between major elements Ca/Mg vs. Cl/SO<sub>4</sub> in the analyzed groundwater samples (1995, 2012, 2015 and 2017)

##### Na vs. Cl

The Na versus Cl relationship has frequently served as a pivotal tool for unravelling the intricate mechanisms behind mineralization acquisition in arid and semi-arid regions (Dixon and Chiswell, 1992; Guo et al., 2019; Bahir et al., 2021).

The aquifer system showed a compelling correlation between Na and Cl (Fig. 7), which strongly suggests the dissolution of halite (NaCl) by groundwater. This means that the two minerals probably have the same origin, and this hypothesis is supported by the negative values of the halite saturation index (SI-Halite) (Fig. 17), thus suggesting halite dissolution as a major process in the study area (Yang et al., 2019; Ouarani et al., 2020).

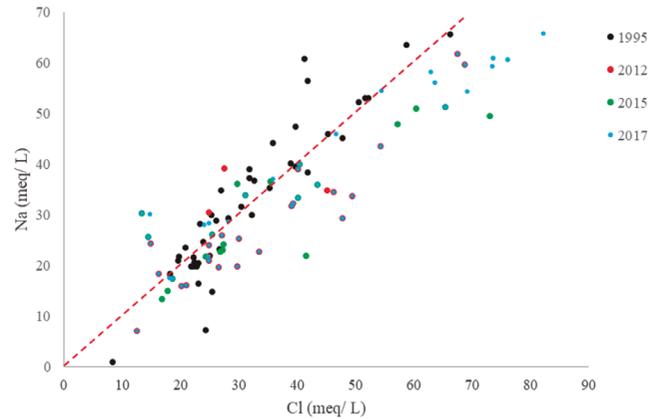
It is noted that there exists excess sodium content in the wells from the years 2012-2015 which are characterized by chloride-sodium facies (Fig. 6). The majority of these water points are located in the Chott Merouane area, which explained the existence of another origin for the sodium ions (irrigation water and water contaminated by the dissolution of salts in the surface crust and the dissolution of chemical fertilizers) thus increasing the concentration of sodium compared to that of chlorides (Houari, 2020).

The surplus of Cl relative to Na can be attributed to the phenomenon of cation exchange. In this phenomenon, Na is fixed and Ca and Mg are released from the aquifer matrix (Hem, 1985; Ouarani et al., 2020). The NaCl chemical facies indicates possible dissolution of salt minerals. It is generally the characteristic of sedimentary terrains containing evaporite sequences (halite, sylvinite) (Klimchouk, 2000; Zakaria et al., 2015), which is confirmed by the geological background of the study area.

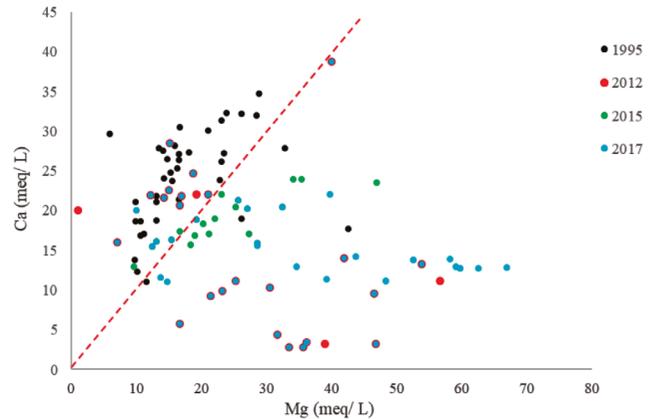
##### Ca vs. Mg

The Ca vs Mg correlation shows a robust positive correlation (Fig. 8), indicating that these two elements likely have the same origin. The excess in

calcium levels in the waters sample for 1995 is explained by the presence of the chloride and sulfate calcium facies, which characterizes these waters (Fig. 6).



**Figure 7.** Correlation Diagram (Na vs. Cl) in the analyzed groundwater samples (1995, 2012, 2015 and 2017)



**Figure 8.** Correlation Diagram (Ca vs. Mg) in the analyzed groundwater samples (1995, 2012, 2015 and 2017)

##### Ca vs. SO<sub>4</sub>

The Ca versus SO<sub>4</sub> correlation diagram (Fig. 9) shows that the majority of samples are located below the gypsum and/or anhydrite dissolution line, reflecting an excess of SO<sub>4</sub> over Ca. The depletion of Ca content in comparison to SO<sub>4</sub> concentration can be attributed to various processes. These processes include: a) cation exchange reactions, wherein calcium ions are adsorbed into clay minerals while sodium ions are simultaneously released, and b) incongruent dissolution of dolomite and gypsum, accompanied by the simultaneous precipitation of calcite (Bischoff et al., 1994; Appelo and Postma, 2005; Jacobson et al., 2010), and/or c) precipitation of carbonates due to CO<sub>2</sub> degassing. (Zakaria et al., 2015; Pisciotta, 2019; Ouarani et al., 2020; Bahir et al., 2021).

##### Ca vs. HCO<sub>3</sub>

The representation of the relationship between Ca and HCO<sub>3</sub> using a regression line of slope equal to 1 (Fig. 10) shows that the groundwater sample points are above the line, thus indicating that the origin of Ca may come from the dissolution of calcite and/or cation exchange reactions. (Clark and Fritz, 1997; Jin et al., 2010; Bahir et al., 2021). Regarding bicarbonates, they do not influence the chemistry of the studied waters, the sources generating HCO<sub>3</sub> are very low or the bicarbonate salts are oversaturated and are in the solid phase (Fig. 13) (Houari, 2020).

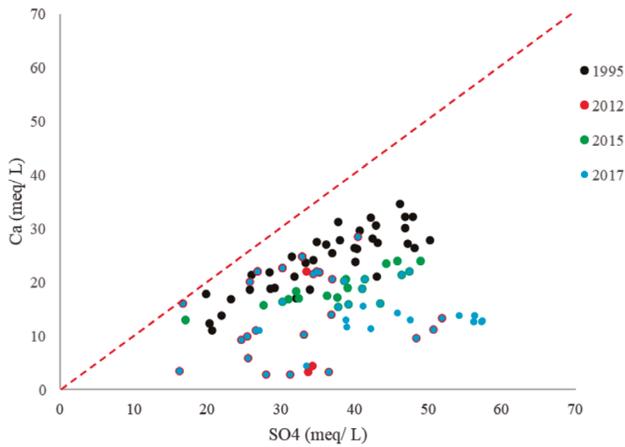


Figure 9. Correlation Diagram (Ca vs. SO<sub>4</sub>) in the analyzed groundwater samples (1995, 2012, 2015 and 2017)

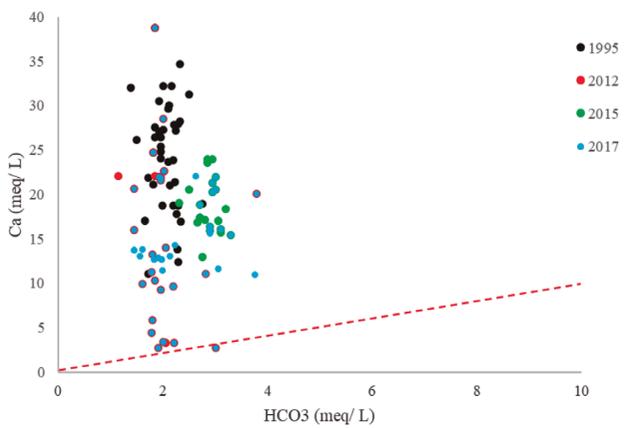


Figure 10. Correlation Diagram (Ca vs. HCO<sub>3</sub>) in the analyzed groundwater samples (1995, 2012, 2015 and 2017)

**Gibbs diagram**

The interaction between groundwater and rocks in the aquifer environment plays a significant role in terms of groundwater quality, providing insights into the development of water chemistry. The Gibbs diagram is widely used to determine the relationship between water compositions and rock properties in underground reservoirs (Gibbs, 1970 ; Annapoorna and Janardhana, 2015 ; Hamidi et al., 2023). Additionally, it is considered in the hydrogeochemical analysis of groundwater to explain the impacts of geochemical processes. The Gibbs ratio is calculated using the following equations ;

$$\text{Gibbs ratio I (for anion)} = \text{Cl} / (\text{Cl} + \text{HCO}_3)$$

$$\text{Gibbs ratio II (for cation)} = \text{Na} / (\text{Na} + \text{Ca})$$

Cl; Chlorine, HCO<sub>3</sub>; Bicarbonate, Na; Sodium, and Ca; Calcium.

Figure 11 presents a Gibbs diagram based on the Total Dissolved Solids (TDS) values of groundwater samples, as well as the Na/(Na+Ca) cation ratio and Cl/(Cl+HCO<sub>3</sub>) anion ratio. According to this diagram, it is observed that Na<sup>+</sup> predominates over Ca<sup>2+</sup> in the cation distribution of the waters, indicating a greater interaction with sodium-rich rocks in the groundwater. In the majority of samples, the Na/Ca ratio is greater than 0.5, signifying a significant increase in Na/(Na+Ca) values and suggesting ion exchange. The diagram shows that

most cations and anions plot within the rock dominance field, indicating that groundwater chemistry is primarily influenced by water–rock interactions and the dissolution of minerals within the lithological formations of the study area. Some samples, however, fall within the evaporation domain, reflecting the influence of evaporite mineral dissolution, particularly halite (NaCl) and gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O), on groundwater mineralization in the Wadi Righ region.

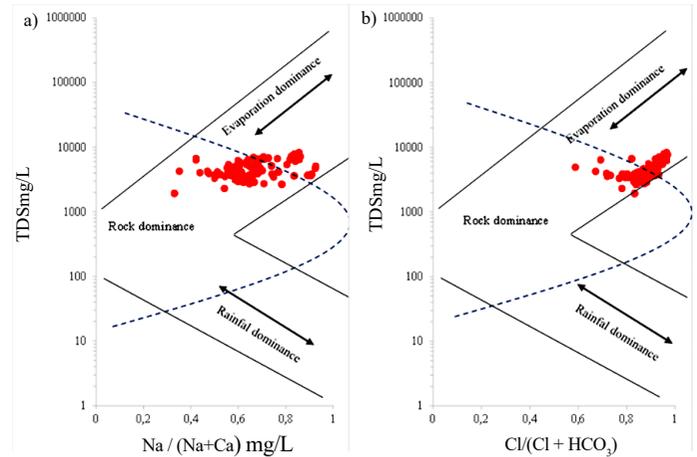


Figure 11. Classification of Terminal Complex groundwater samples according to the Gibbs diagram (1995, 2012, 2015, and 2017)

**Saturation indices**

Figure 12 represents the evolution of the saturation indices of the waters of the Terminal Complex aquifer over time (from 1995 to 2017); these indices are Anhydrite (CaSO<sub>4</sub>), Aragonite (CaCO<sub>3</sub>), Calcite (CaCO<sub>3</sub>), Dolomite (CaMg(CO<sub>3</sub>)<sub>2</sub>), Halite (NaCl), and Gypsum (CaSO<sub>4</sub>·2H<sub>2</sub>O). These dissolved mineral saturation indices show the sensitivity of carbonate minerals (dolomite, calcite, and aragonite) to precipitation. This is also the case for evaporite minerals, namely gypsum and anhydrite. Carbonate minerals have different saturation indices, calcite varies from -0.44 to 2.01, followed by aragonite, which ranges from -0.59 to 1.86, and finally dolomite, which ranges from -1.14 to 4.52 (Fig. 13). It can be said that the three elements have reached their supersaturation state in most of the analyzed waters.

The evaporative minerals, specifically gypsites, undergo precipitation after the less soluble carbonates. The gypsum and anhydrite from evaporative minerals show saturation indices with negative values that range from -1.35 to 0.2 and -1.66 to -0.1 respectively (Fig. 13), reflecting the contribution of gypsum and anhydrite to the mineralization of groundwater (Bahir et al., 2021). Despite the dominance of the chemical components (Na and Cl) in concentration in some samples, halite, whose saturation indices vary from -6.88 to -4.1, remains undersaturated (Idder et al., 2016).

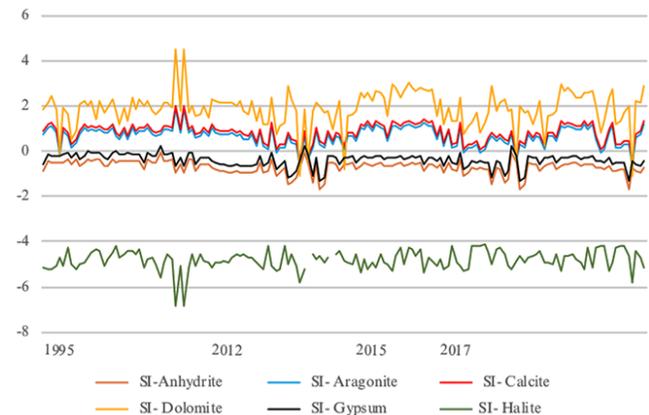


Figure 12. Saturation indices of minerals related to interactions with water samples

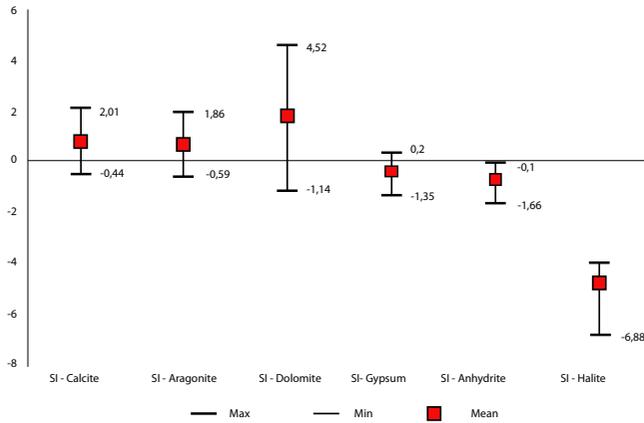


Figure 13. Min-Max and Mean values of saturation indices from Terminal Complex aquifer

According to the spatial distribution figures of indices in the Wadi Righ region (Fig. 14, 15 and 16), the average values of saturation indices (SI-Calcite, SI-Aragonite, and SI-Dolomite) have decreased over the years. Although they are still in a state of oversaturation, their values range from 0.98 (1995) to 0.66 (2017) for SI-Calcite, 0.84 (1995) to 0.51 (2017) for SI-Aragonite, and 1.92 (1995) to 1.76 (2017) for SI-Dolomite. The Gypsum and Anhydrite indices decreased with very low percentages, ranging from -0.21 (1995) to -0.49 (2017) for SI-Gypsum and -0.52 (1995) to -0.79 (2017) for SI-Anhydrite, while the values of SI-halite gradually increased from -4.91 (1995) to -4.72 (2017).

The precipitation of carbonate minerals (calcite, aragonite, and dolomite) and the dissolution of evaporite minerals (gypsum, anhydrite and halite) increases from north to south (Fig. 14, 15 and 16), and this as a result of the slow movement of water flow in the south of the Wadi Righ region in general; this means that the residence time of groundwater in aquifers results in a longer time for water/rock interactions to occur and for minerals to equilibrate between groundwater and host rocks (Edmunds et al. 2003, Gurmessa et al. 2022).

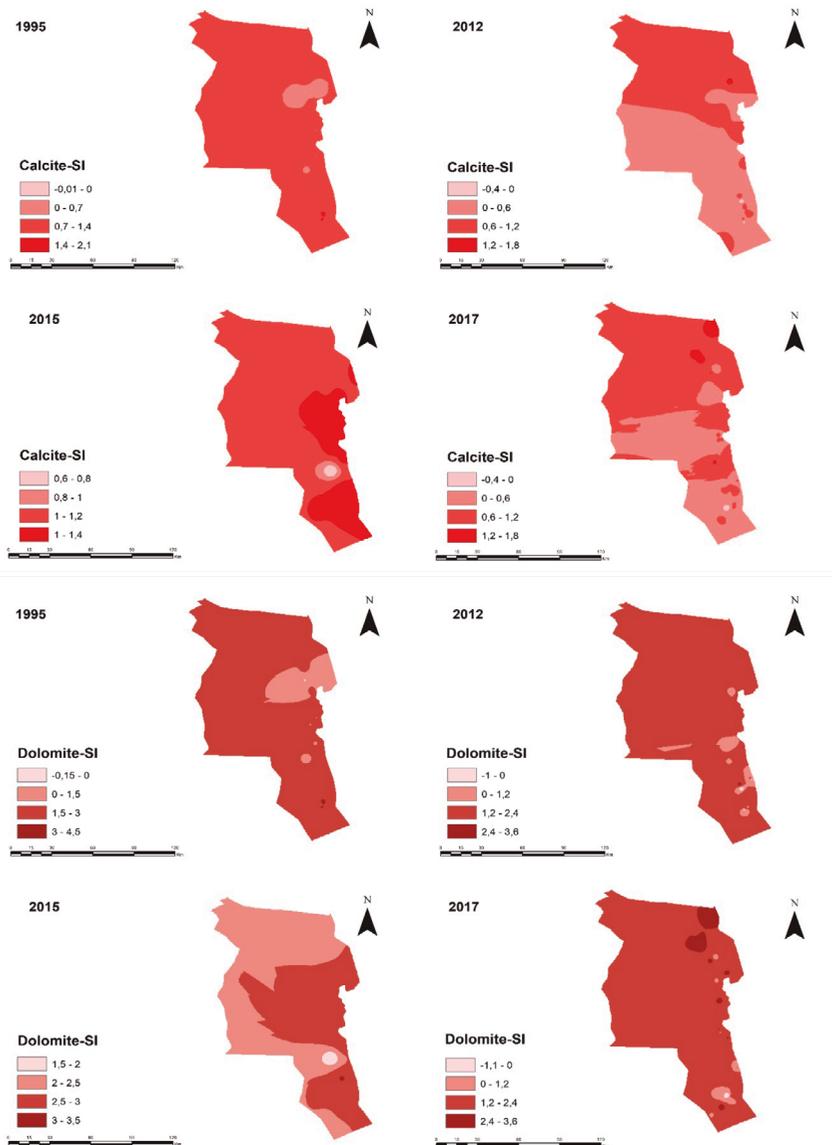


Figure 14. Spatial distribution of saturation indices (1995, 2012, 2015 and 2017); SI-Calcite and SI-Dolomite

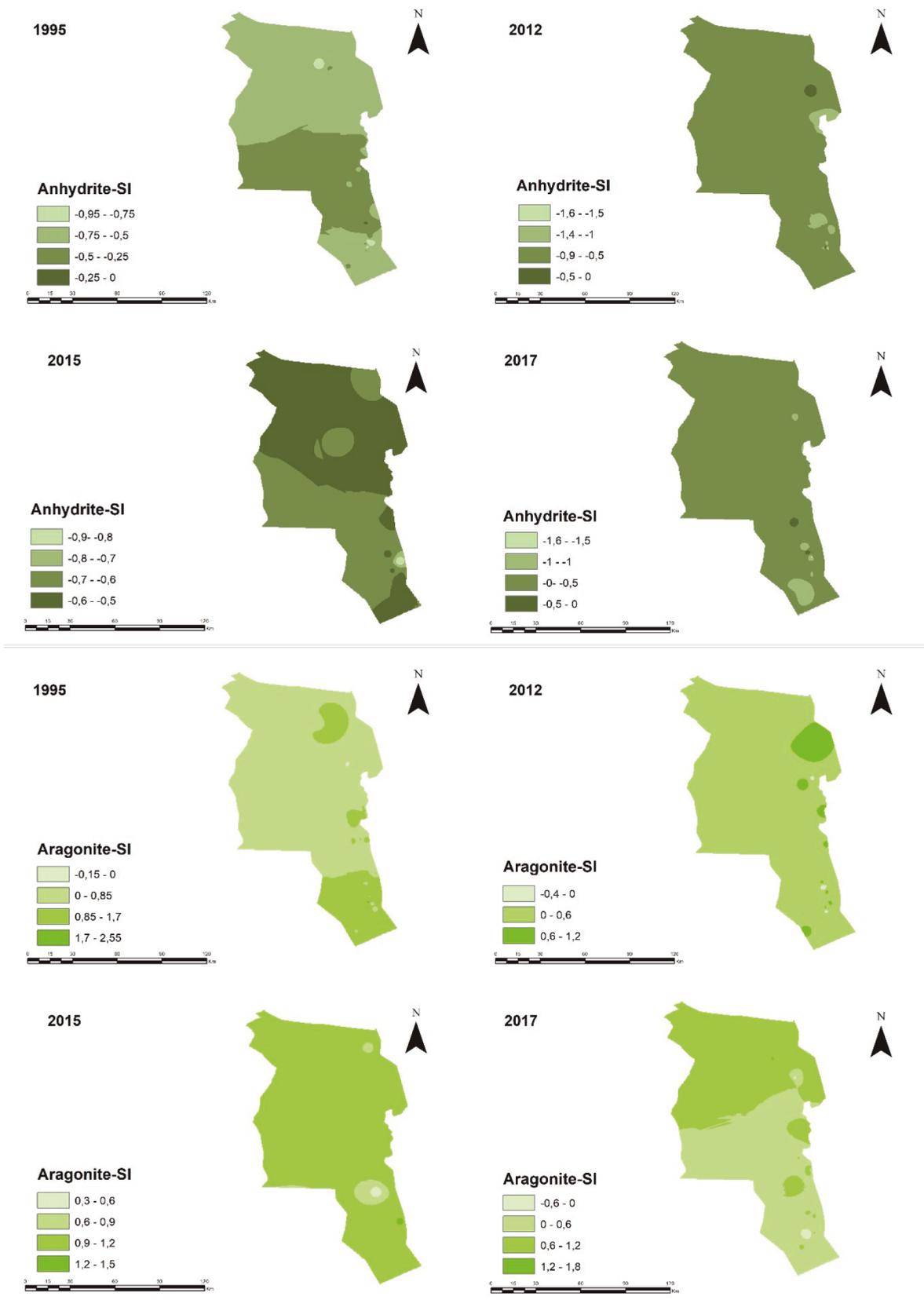


Figure 15. Spatial distribution of saturation indices (1995, 2012, 015 and 2017); SI-Anhydrite and SI-Aragonite

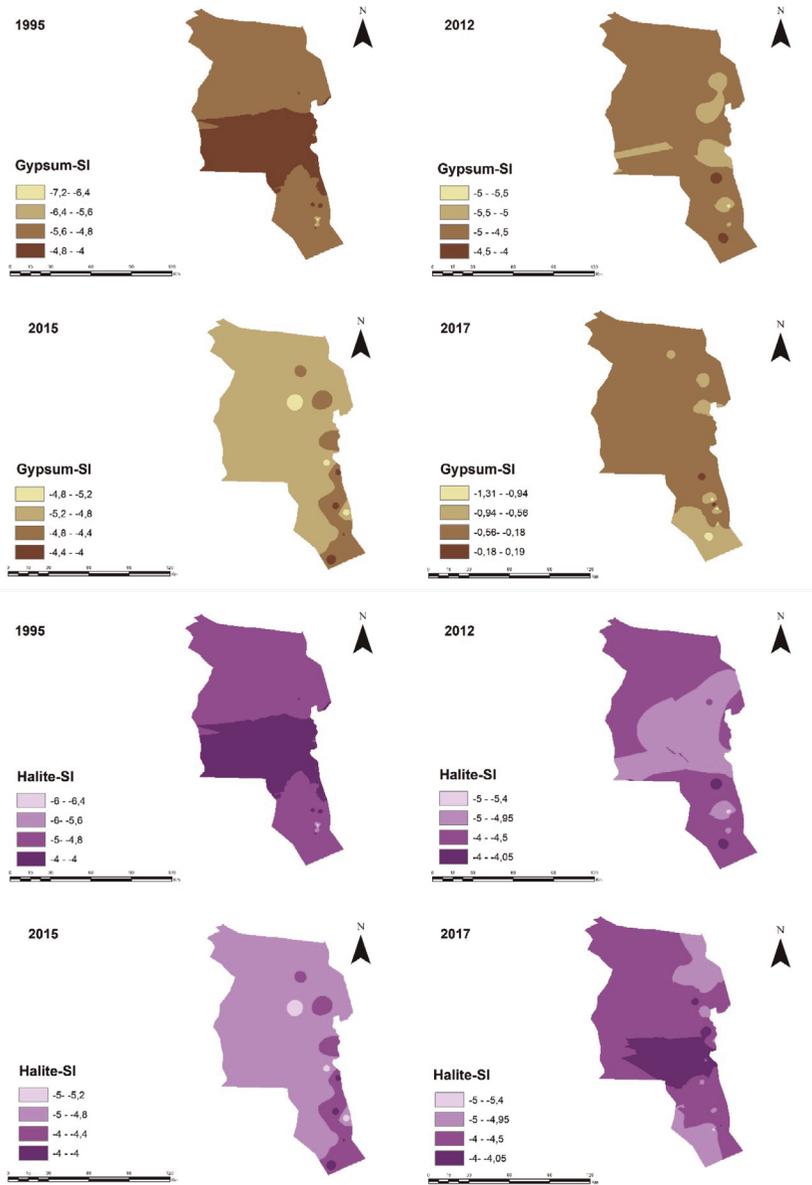


Figure 16. Spatial distribution of saturation indices (1995, 2012, 2015 and 2017); SI-Gypsum and SI-halite

**Hierarchical cluster statistical analysis (HCA)**

Based on the HCA classification (Fig. 17), The first group encompasses subsection 1.1, which delves into bicarbonates and potassium. It elucidates that bicarbonate has the potential to vie with potassium for sorption sites on minerals in the subsurface. This competitive interaction could result in the liberation of potassium into the groundwater as concentrations of bicarbonate escalate.

On the other hand, branch 1.2 comprises chloride, sodium, and magnesium, which constitute the chemical facies of the water obtained earlier and connects with halite, attributing the source of chloride and sodium in the water to it. The correlation of this group with Total Dissolved Solids (TDS) arises from the fact that these elements are the fundamental contributors to the mineralization of water in the studied samples.

The second group is divided into two sections. The correlation between  $SO_4^{2-}$  and  $Ca^{2+}$  with electrical conductivity signifies the impact of evaporated rocks on the salinity of water in this region. Gypsum and anhydrite are associated with calcium in group 2.1, which, in turn, connects to section 2.2. This linkage is because calcium (Ca) is a major component present in three minerals: aragonite ( $CaCO_3$ ), calcite ( $CaCO_3$ ), and dolomite ( $CaMg(CO_3)_2$ ).

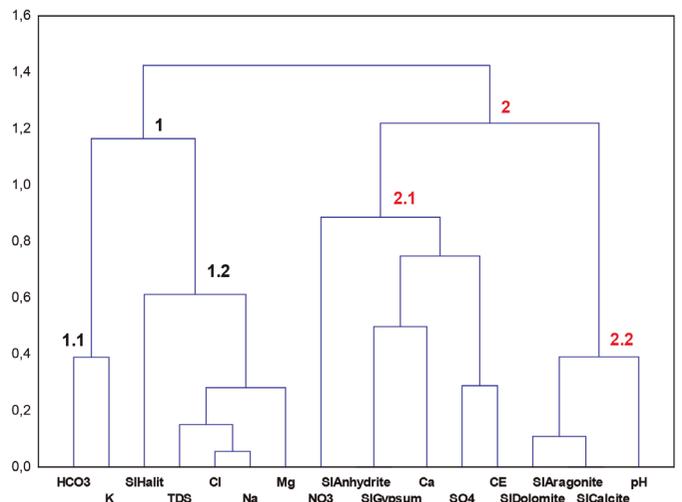
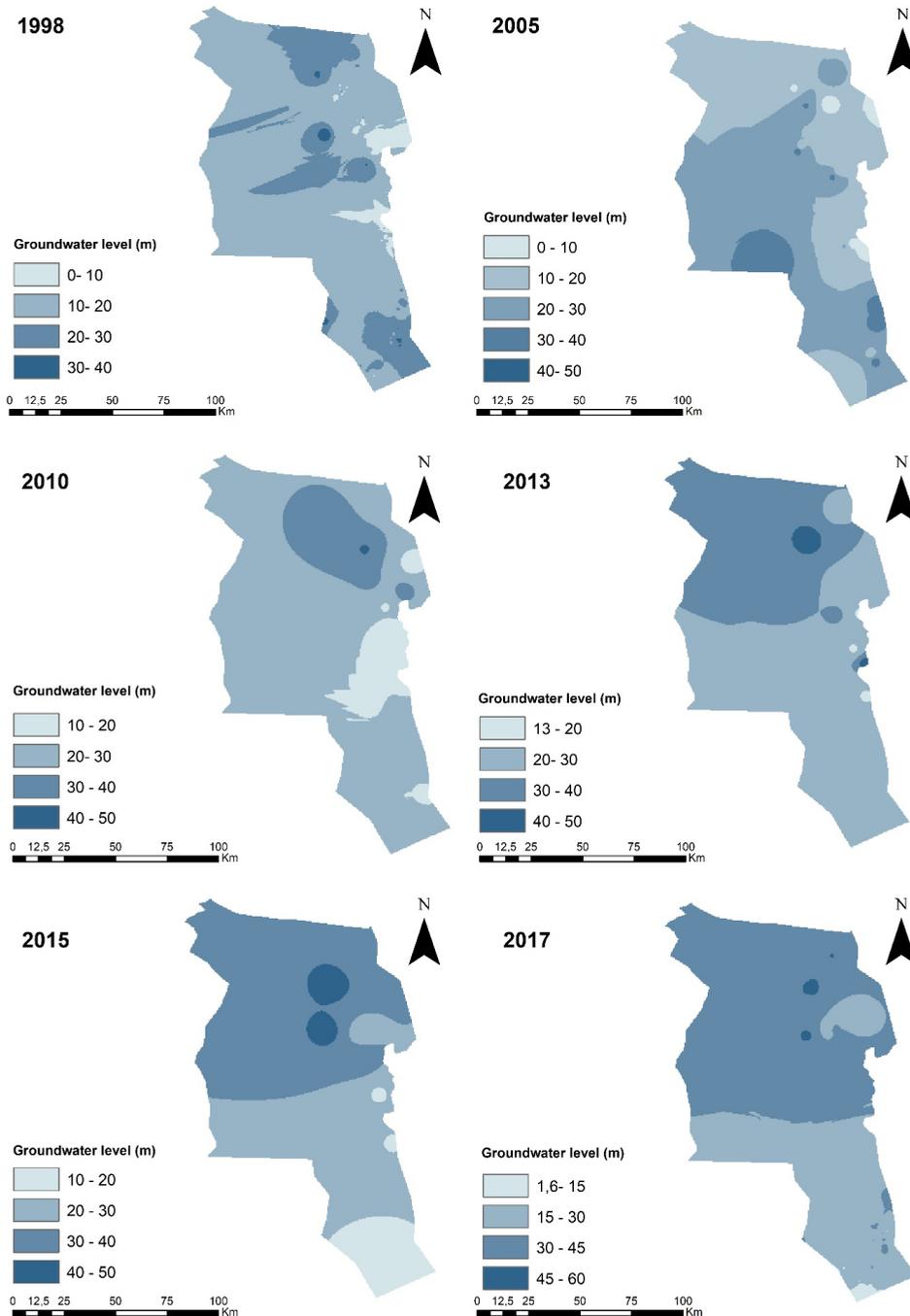


Figure 17. Cluster analysis results of physicochemical variables of the Complex Terminal groundwater in the Wadi Righ area

*Spatial and temporal evolution of the groundwater levels of groundwater in the terminal complex aquifer*

The spatial evolution of the groundwater level (Fig. 18) shows a flow direction following the topographic model of the region. The general direction begins from the south to the north (where the natural outlet are located “Chott Merouane”), or towards areas of overexploitation, indicating the main palm groves and the urban areas. In recent years (2010-2013-2015-2017), there has been a noticeable rise in water levels in the southern and central areas (palm grove zones) of the region. This rise may be accelerated by the infiltration of irrigation water and waste water at the irrigation network level into the aquifer (Zahi et al., 2011).

The groundwater level of the Terminal Complex decreased by approximately 14.7 meters (Fig. 19) between the years 1998 and 2017 ( $L_{max} = 35.6$  m in 1998 compared to  $L_{max} = 50.3$  m in 2017). This is consistent with the results of the (OSS, 2003) report, which predicted, through simulation, a decrease in the groundwater level of the Terminal Complex aquifer by about 30 meters by the year of 2050. This decrease can be explained by the intensive exploitation of the aquifer (Barrez et al. 2004; Jamaa et al. 2017) and by a supply deficit being a result of the successive drought years, and the noticeable climate changes that the world and the Wadi Righ region in particular are experiencing (MacDonald et al., 2012; Bettahar and Şener, 2022).



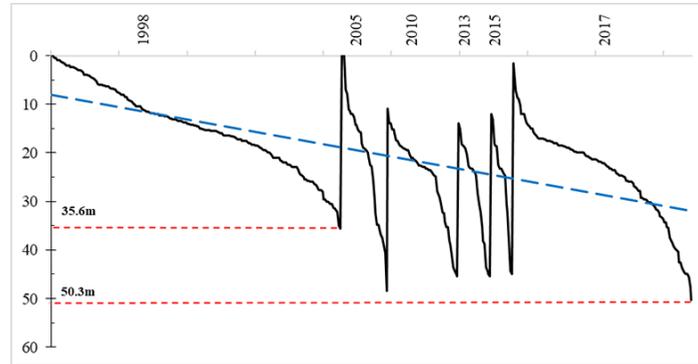
**Figure 18.** Evolution of groundwater levels map of the Terminal Complex in the Wadi Righ (1998, 2005, 2010, 2013, 2015 and 2017)

*Spatial and temporal evolution of groundwater mineralization*

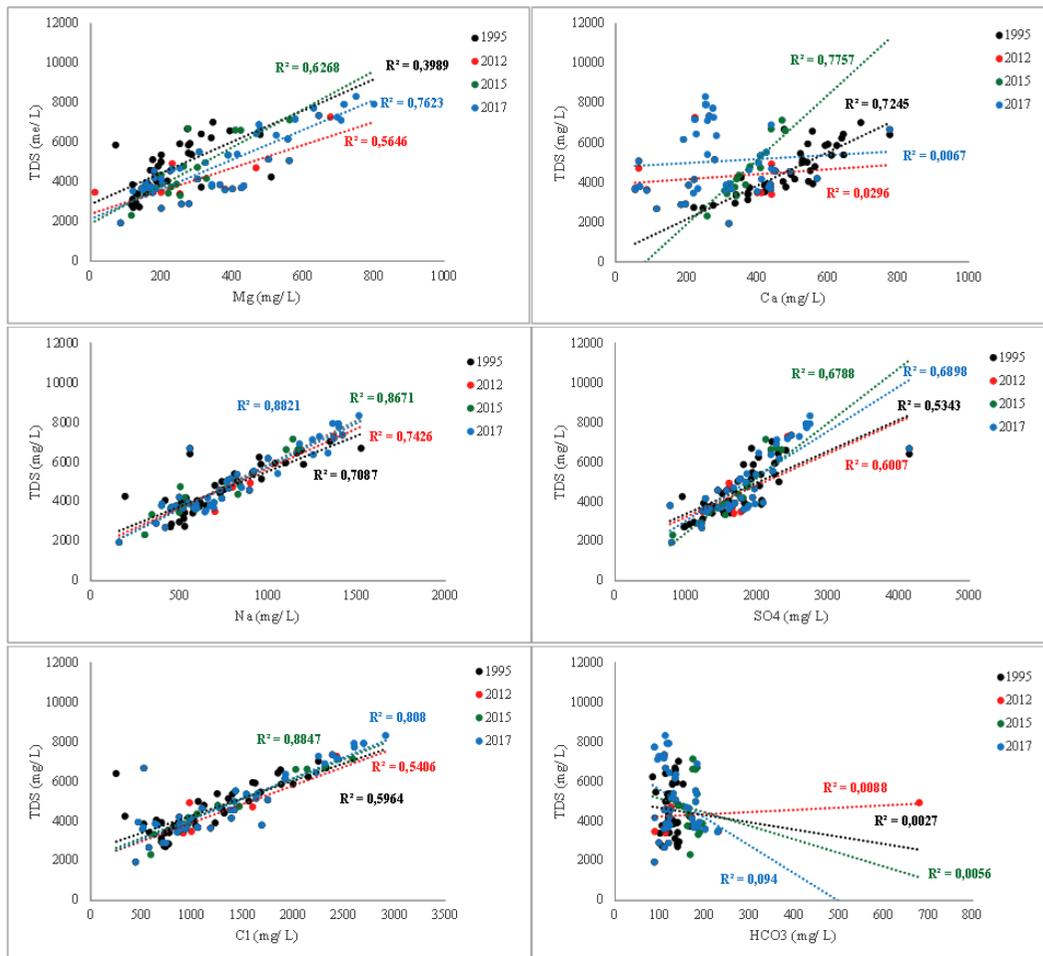
Upon analyzing the relationship between chemical elements and total mineralization (TDS) (Fig. 20), it becomes evident that the variability of the latter (TDS) is primarily influenced by chloride, sulfate, magnesium, and sodium, with correlation coefficients ( $R^2$ ) of 0.59, 0.54, 0.88, and 0.8 for chloride, 0.7, 0.74, 0.86, and 0.88 for sodium, 0.39, 0.54, 0.62, and 0.76 for magnesium, and 0.53, 0.6, 0.67, and 0.68 for sulfate. These elements are pivotal factors contributing to the mineralization of water in the samples under investigation (Zakaria et al., 2015).

The total dissolved solids (TDS) value is a useful indicator of the mineralization degree of water. Since electrical current is transported by ions in the solution, conductivity increases as the ion concentration increases

(Hiscock and Bense, 2014). The average TDS values of groundwater in the Terminal Complex (Table 1 and Fig. 21) range from 4303.59 to 5052.17 mg/L. Approximately, 90.47%, 81.47%, 95.23%, and 94.23% (1995, 2012, 2015, and 2017, respectively) of the samples are highly mineralized ( $>3000$  mg/L). It is generally observed that the electrical conductivity values exceeded potability standards ( $>1000$   $\mu\text{S}/\text{cm}$  for highly mineralized) (Gurmesa et al., 2022; Al Haj et al., 2023). The conductivity values ranges from 4300 to 11200  $\mu\text{S}/\text{cm}$  for the year 1995, from 2760 to 11200  $\mu\text{S}/\text{cm}$  for the 2012 campaign, from 2440 to 7560  $\mu\text{S}/\text{cm}$  for 2015, and from 2800 to 9030  $\mu\text{S}/\text{cm}$  for the year 2017 (Table 1). The electrical conductivity and TDS values generally change along the flow direction (from South to North) (Fig. 13) and they also increase in palm tree areas (Bettahar et al., 2017b).



**Figure 19.** Evolution of groundwater levels of the Terminal Complex in the Wadi Righ (1998, 2005, 2010, 2013, 2015 and 2017)



**Figure 20.** Relationship between major chemical elements and total mineralization (TDS) (mg/L)

The decrease in the groundwater level of the aquifer (Fig. 22) is accompanied by a slight decrease in conductivity and an increase in mineralization over time. This is due to a clear inverse correlation between groundwater recharge and conductivity (Gurmessa et al., 2022). It's important to note that the evolution of the water table level can be influenced by many factors, such as precipitation, irrigation, water resource exploitation, and human activities (Ouarani et al., 2020). Anthropogenic impact, such as unplanned

pumping in the region, can have a significant effect on groundwater levels by increasing the volume of water leaving the aquifer and decreasing its recharge. Regions with low to very low recharge in North Africa are generally characterized by variable salinities with more frequent salty groundwater wells (high mineralization) (Bettahar et al., 2017b; Houari, 2020; Gurmessa et al., 2022; Al Haj et al., 2023).

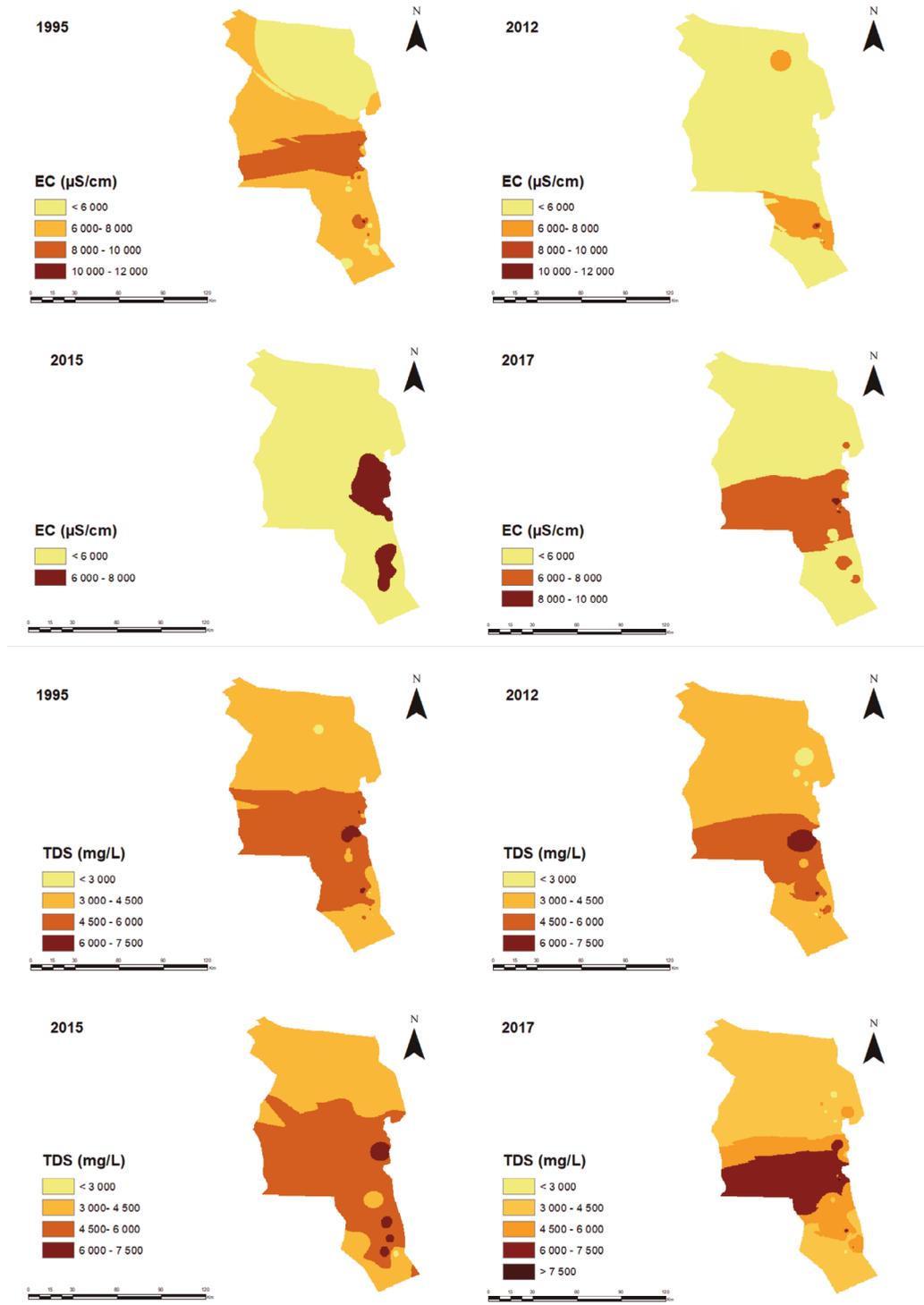
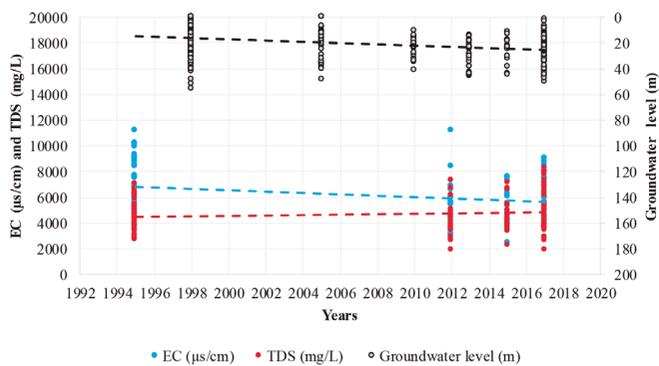


Figure 21. Spatial distribution of electrical conductivity and TDS in the Terminal Complex aquifer of the Wadi Righ (1995, 2012, 2015, and 2017)

**Table 1.** Elementary Statistics of Electrical Conductivity ( $\mu\text{s}/\text{cm}$ ) and TDS ( $\text{mg}/\text{L}$ ) of groundwater in the Terminal Complex aquifer (1995, 2012, 2015, and 2017)

		EC ( $\mu\text{s}/\text{cm}$ )	TDS ( $\text{mg}/\text{L}$ )	pH
1995	Min	4300	2711	7.4
	Max	11200	7011	8.4
	Average	6974.42	4591.57	8.03
2012	Min	2760	1934	6.76
	Max	11200	7346	8.71
	Average	5554.14	4303.59	7.87
2015	Min	2440	2310	7.65
	Max	7560	7130	8.49
	Average	5143.48	4641.13	8.22
2017	Min	2800	1934	6.76
	Max	9030	8318	8.71
	Average	5981.85	5052.17	7.98

**Figure 22.** Correlation between groundwater level, electrical conductivity and total dissolved solids (TDS) of the Terminal Complex aquifer

#### 4. Conclusion

This study examined the spatiotemporal evolution of groundwater mineralization in the Terminal Complex aquifer of the Wadi Righ region using extensive hydrochemical datasets. The results revealed that groundwater is highly mineralized, with very high electrical conductivity values. The dominant processes controlling mineralization are the dissolution of evaporite minerals particularly gypsum, anhydrite, and halite and inverse cation exchange between groundwater and aquifer materials.

The saturation indices indicate undersaturation with respect to sulfate minerals, highlighting their dissolution as a major contributor to groundwater salinity. In contrast, the oversaturation of carbonate minerals (calcite, dolomite, and aragonite) reflects ongoing precipitation processes. These patterns intensify from north to south due to longer groundwater residence times and slower flow rates, which promote stronger water–rock interaction in the southern parts of the aquifer.

Groundwater chemistry is dominated by calcium–magnesium chloride–sulfate facies, resulting from the dissolution of the surrounding geological formations and prolonged contact between water and rocks. The spatial analysis of piezometric levels revealed a general groundwater flow from south to north, directed toward zones of intensive pumping around major palm groves and urban centers. These areas are characterized by declining water levels due to excessive extraction and insufficient recharge during dry periods.

Finally, the observed decline in groundwater levels and the increase in mineralization highlight the need for sustainable water management practices. Continuous monitoring of the Terminal Complex aquifer is essential to mitigate overexploitation and to preserve groundwater quality and availability for agricultural, domestic, and ecological needs under growing climatic and anthropogenic pressures.

#### Acknowledgments

The authors would like to thank the Algerian Water Company (ADE) and the National Water Resources Agency (ANRH) for providing the necessary data for the preparation of this research work.

#### Funding

No funding was received in the preparation of this manuscript.

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