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GROUNDWATER INVESTIGATION IN SAHARAN AREAS USING STATISTICAL AND STABLE ISOTOPE APPROACHES – EL GOLEA CENTRAL SOUTH OF ALGERIA CASE STUDY

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Summary

Groundwater quality determination and age estimation in a desert landscape of El Golea province situated in the south of Algeria has been investigated in the present research paper. For this regard, 57 water samples were collected from an aquifer composed of two superimposed systems; phreatic and deep continental intercalary (CI) aquifers which are a part of the Northern Sahara Aquifer System (NWSAS). Samples were analyzed to assess the age and water quality using descriptive, multivariate statistics (PCA and HCA) and stable isotopes. It is revealed that more than 71% of the IC points are characterized by a water type $(Ca^{2+}, Mg^{2+}) (HCO_3^-)_2$ and more than 83% of the TC samples are defined by a water type $(Ca^{2+}, Na^+) (HCO_3^-, SO_4^{2-})$ and very high salt ions contents due to the influence of surface water, evaporate leaching and irrigation water return. The isotopic composition of samples of phreatic and CI aquifers shows a clear difference between the two qualities of water. The phreatic aquifer is characterized by the δ18O range from –4.68 to –6.1, whereas δ2H from –47.25 to –59.48 and CI with values of the δ18O range from –5.96 to –7.6, and δ2H range between –53.7 and –65.78 isotopic signature. The unconfined aquifer above IC forms a special case of a mixture of ancient water from deep horizons and recent water strongly enriched from shallow horizon lands.

Key words

1. Introduction

The studied area is a part of the North-Western Sahara Aquifer System (NWSAS), one of the largest in the world. It consists of two main aquifers, the Continental Intercalary (CI) and the Terminal Complex (TC), which are shared by three countries. It covers an area of about 700,000 km², of which 60% is in Algeria. The CI is the thicker of the two aquifers and has the larger surface area. However, the CI aquifer also more exploited than the TC aquifer. There is limited interaction between the aquifers [Edmunds et al. 2003]. Both the CI and phreatic aquifer systems have been the subject of several hydrogeochemical studies published over past decades

[Darling et al. 2018, Hakimi et al. 2021, Fenazi et al. 2022]. Domestic and agricultural needs in the El Golea region are met by groundwater from both aquifers. In order to control and assess the water quality, it is necessary to understand the hydrogeochemical characteristics of the water and to ensure that the levels of chemical ions do not exceed the standards set by the WHO (World Health Organization). High concentrations of ions in water can cause serious problems for humans and the environment [Boucenna et al. 2018]. It is therefore essential to understand the chemistry of groundwater and its suitability for potable water and irrigation. The multiplication of domestic and industrial discharges and agricultural activities in the El Golea area increases the risk of contamination of the IC groundwater through exchange with the overlying free groundwater characterized by poor quality water for domestic and agricultural use [Fenazi 2022].
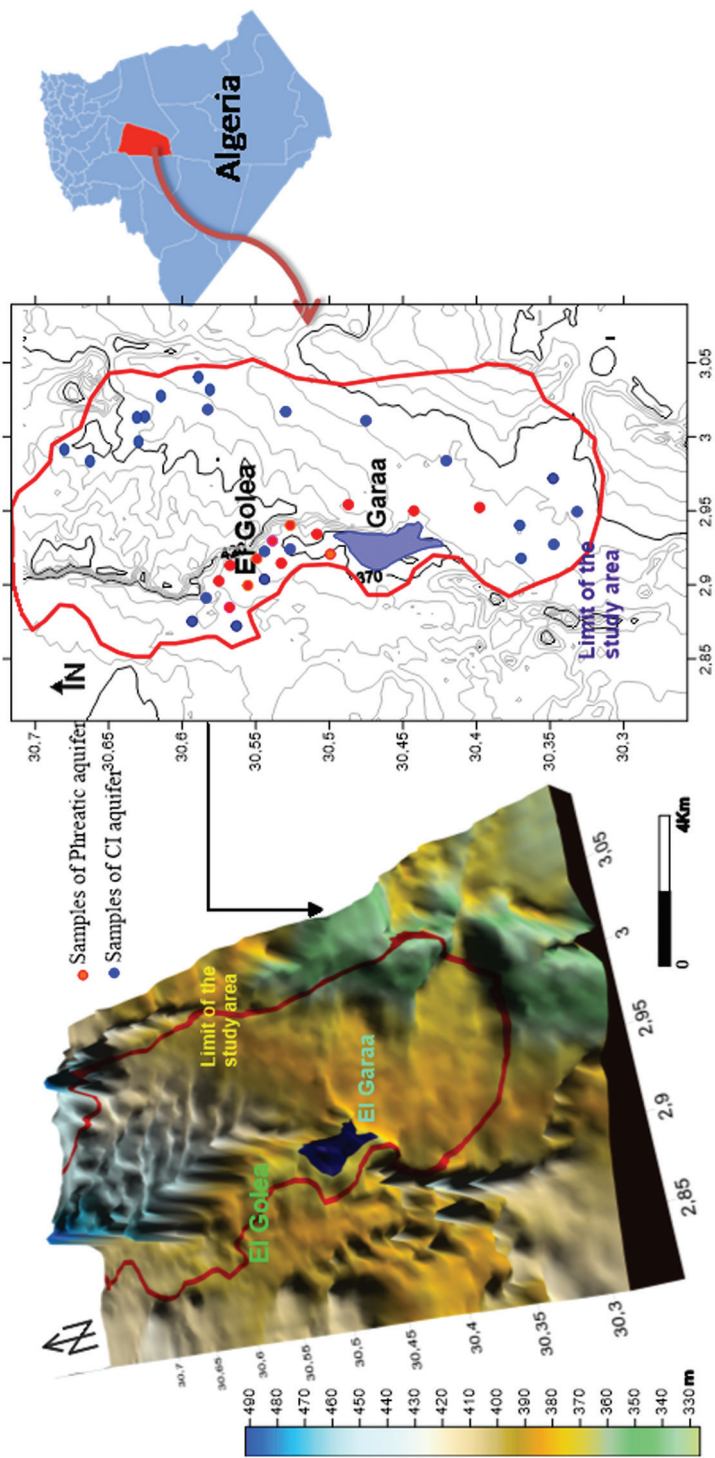
2. Study area

El-Goléa region covers an area of 49,000 km². It is an oasis attached to the wilaya of Ghardaïa. Characterized by a hyper-arid climate with an average temperature exceeding 22°C and an average rainfall of 171.3 mm/year, the study area is located at latitude of 30°35' North and a longitude of 02°52' East, its average altitude reaches 396 m (Fig. 1).

From a geological point of view (Fig. 2), there are two natural structures in this area that are characteristic of the desert environment. The lower Cenomanian cliffs and plateaus are made up of limestone and grey, marl with intercalation of variegated clay. The plain or elongated depression, formed by Albian and Quaternary overlying marls, sandstones and red vraconian sands, the deposit of continental Quaternary shows thickness that varies zonally.

Hydrogeologically, the study area lies within the Albian aquifer, which consists of two superimposed aquifers, the free aquifer and the continental intercalary aquifer. The piezometric level is very close to the surface. It is less than 1 meter deep, causing problems due to the rise of water. According to G. Capot-Rey [1958], the phreatic aquifer is located in the Quaternary formations and benefits from the water collected by the Seggueur wadi. It originates in the infiltrations coming either from the artesian water flowing upwards or from the presence of fissured limestone bars in the roof of the Continental Intercalary. It is also fed by the returning irrigation water.

The Albian sands and sandstones are found underneath the clay-limestone layers, which are 20 to 30 m thick and contain a charged aquifer that is the main water resource in the region [Capot-Rey 1958]. The depth of the aquifer varies between 65 and 250 m towards the north.

Source: Authors' own study

Fig. 1. Geography of the study area
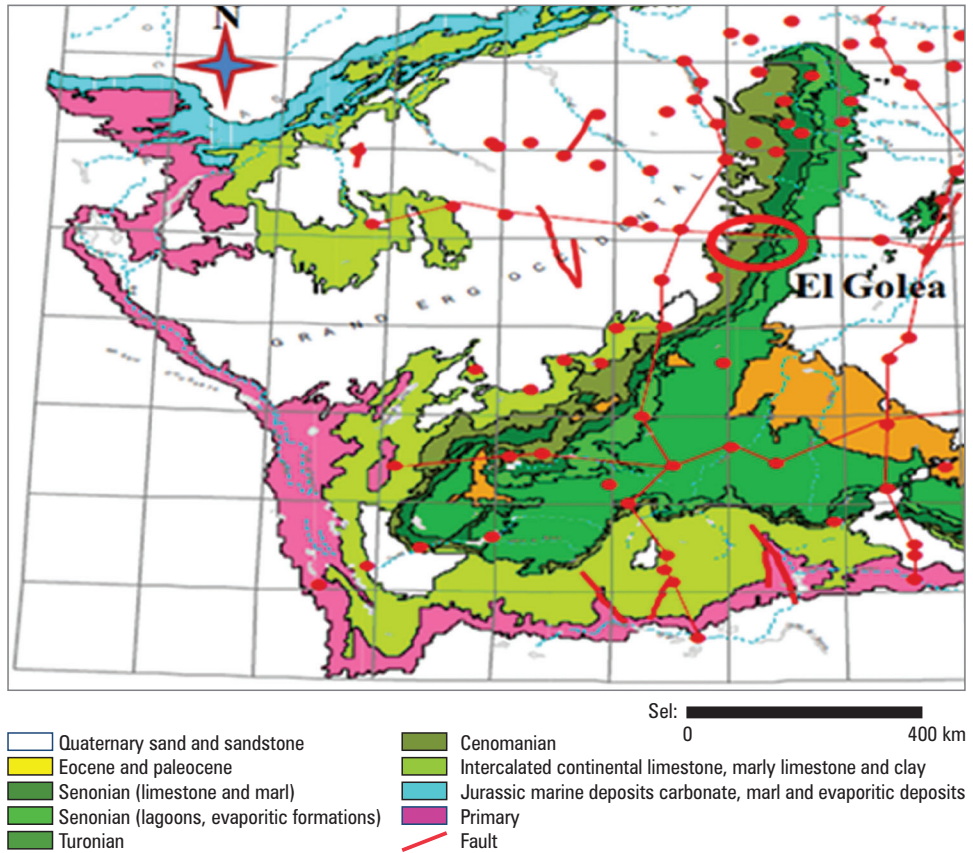
Source: SASS geological map 2003

Fig. 2. Extract from a geological map of the study area

3. Sampling and analysis procedure

Samples of the groundwater in the study area were collected intermittently to observe spatial variations in geochemical and isotopic parameters. A total of 57 samples were taken from the El Golea plain. The samples are distributed as follows: a) 18 samples were taken from wells exploiting the phreatic aquifer. b) 39 samples were taken from the Continental Intercalary aquifer.

PH and temperature measurements were carried out in the field. Chemical analyses and isotopic measurements were carried out at the Laboratory of Radio-Analysis and Environment of the National School of Engineers of Sfax (Tunisia).

- The major elements (Na^+, Mg^{+2}, Ca^{+2}, K^+, Cl^-, SO_4^{-2}, HCO_3^- and NO_3^-) were analyzed by high-performance ionic liquid chromatography for the cations, and a Metrohm chromatograph equipped with CI Super-sep columns for the anions. The overall

detection limit for the ions was 0.04 mg L^{-1}. Stable isotope analyses (^{18}O/^{16}O and ^{2}H/1H) were conducted using the LGR DLT 100 Laser Absorption Spectrometer [Penna et al. 2010].

- In order to identify the most important factors controlling groundwater geochemistry in the El Golea area, Principal Component Analysis (PCA) and Hierarchical Ascending Classification (HAC) were performed using the Statistica 7.0 program.

PCA is applied to standardized data to assess associations between variables. This method highlights the involvement of individual chemicals in several influencing factors, which usually occurs in hydrochemistry. It attempt to simplify the complex and diverse relationships that exist among the set of observed variables by revealing common [Evans et al. 1996].

Hierarchical Clustering (HCA) involves repeatedly grouping individuals, starting at the bottom (the two closest individuals) and gradually building a dendrogram so that all individuals are grouped into a single class, at the root. This is called hierarchical classification because each class of a given partition is included in a class of the next partition. The classification result is presented in a graphical form called a dendrogram.

4. Results and discussion

4.1. Statistical treatment

The study of the various correlations established between the concentrations of the main major elements (Cl^{-}, SO$_4^{2-}$, HCO3^{-}, Na^{+}, Ca^{2+}, Mg^{2+}, K^{+} and NO$_3^{-}$) and the total mineralization of the waters (Fig. 3) allowed the origin of the mineralization of the sampled waters to be traced. The presence of a positive correlation between these ions (Cl^{-}, SO$_4^{2-}$, Na^{+}, Ca^{2+} and Mg^{2+}) and the total dissolved salts reflects the participation of these elements in the acquisition of the saline load of the groundwater. This correlation indicates the presence of a common source of mineralization of the waters of the free aquifer and the Continent Intercalary, which can only be the dissolution of evaporates and the alteration of carbonates. This is corroborated by the saturation indices (Is) calculated by the Aquachem 11 program, which show a state of supersaturation for all the samples with respect to calcite and dolomite and a slight undersaturation with respect to gypsum.

Ca^{2+} and Mg^{2+} contents show a large variability, for Ca^{2+} from 5 to 57 mg · L^{-1} in the IC and from 24 to 271 mg · L^{-1} in the phreatic aquifer. For Mg^{2+} from 5 to 37 mg/l in the IC aquifer, and from 26 to 275 mg/l in the unconfined aquifer.

This can be explained by the fact that these two cations may be involved in the processes of dissolution/precipitation of gypsum, calcite and dolomite and in the phenomena of cation exchange and Ca^{2+}, Mg^{2+} exchange due to the interaction between water and dolomitized rocks.

All the analytical points are positioned on the gypsum solution line (Fig. 4), reflecting an excess of Ca^{2+} over SO$_4^{2-}$, which is confirmed by a good correlation between these two elements (correlation coefficient, R = 0.84). Figure 4 shows the good correlation
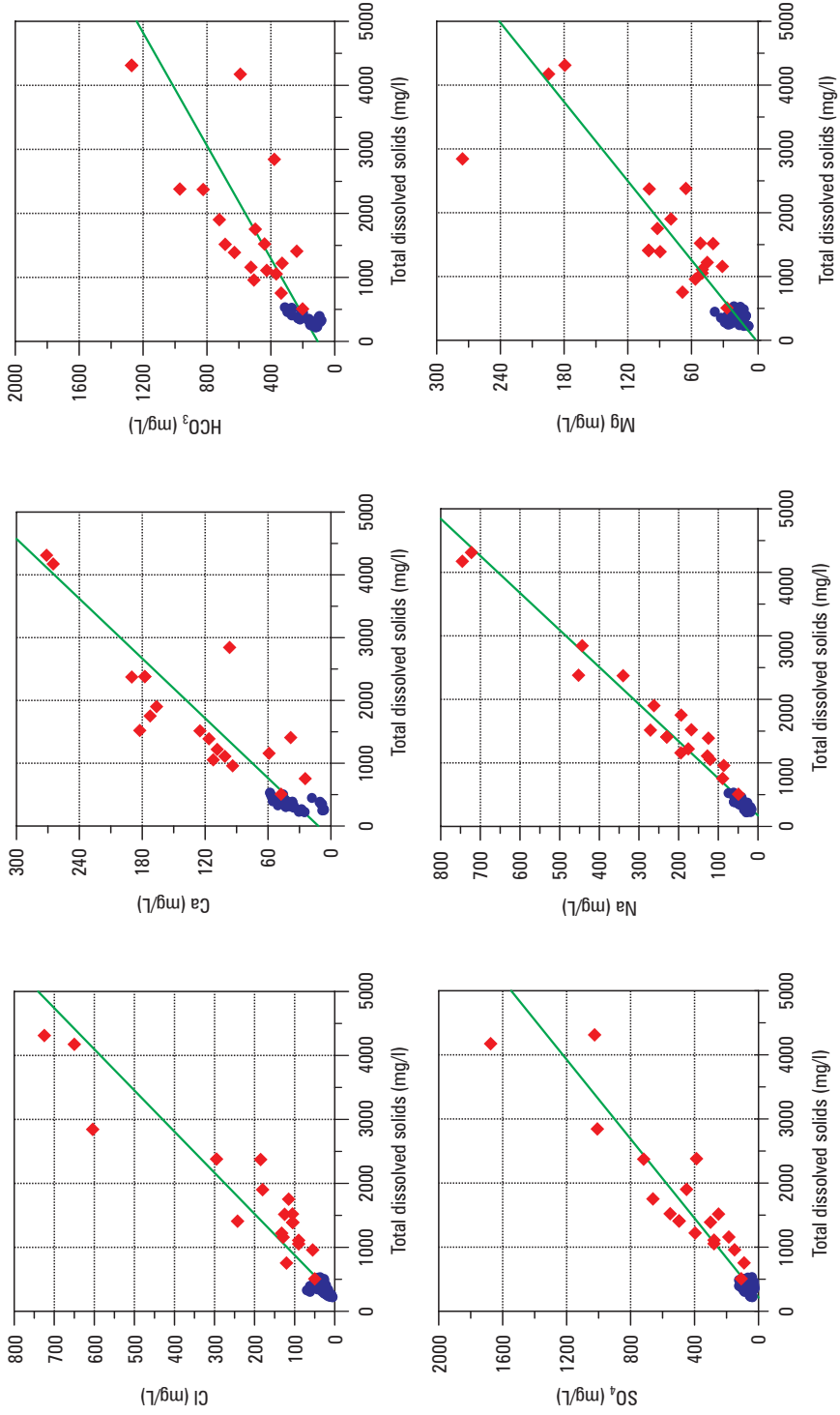
Source: SASS geological map 2003

**Fig. 3.** Relationships between major elements and total dissolved solids
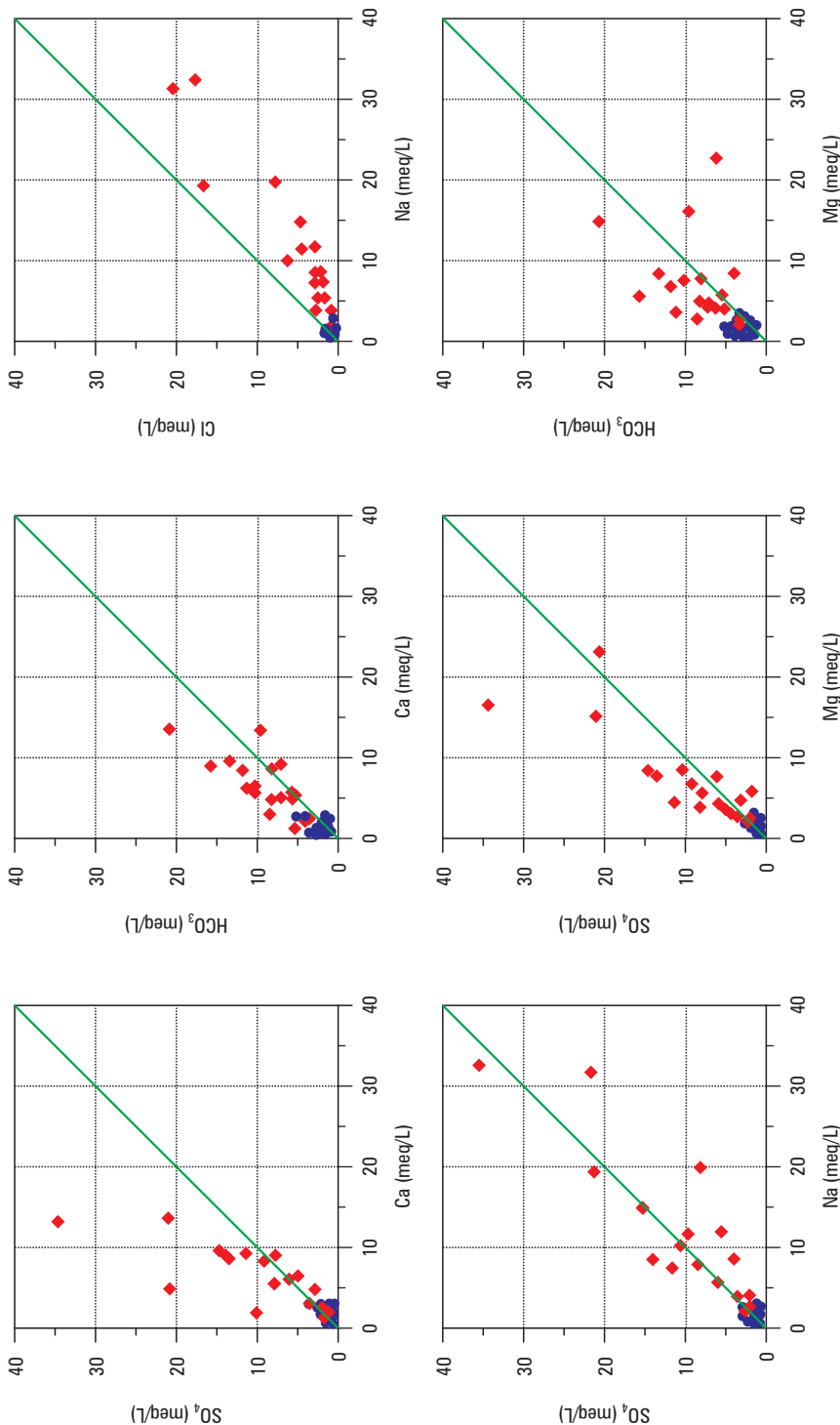
Source: Authors' own study

Fig. 4. Relationships between major elements

between SO_4^{2-} and Mg^{2+} (R = 0.89) and SO_4^{2-} and Na^+ (R = 0.92). Indeed, the majority of the sampling points in both aquifer systems show proportionality and are located on or near the dissolution lines of the exaporite formations ($CaSO_4 H_2O$ gypsum, $NaSO_4$ thenardite, and $MgSO_4$ mirabilite), which is a characteristic lithology of arid and hyper-arid climates. The analytical points that are located on the line of solution of the calcite ($CaHCO_3$) reflect an "excess" in Mg^{2+}, which can be attributed to a secondary precipitation of calcite, to a precipitation of dolomite and/or to an exchange of bases (Ca/Na) and (Mg/Na) on the clay minerals, the intervention of which is suggested by a relative variation of the contents of Na^+ with respect to Cl^-.

The participation of Cl^- and Na^+ ions in the total mineralization of the waters would result from a possible dissolution of the halite (influence of the Sabkha). This is supported by the positive correlation between Cl^- and Na^+, which shows (R = 0.95) in Figure 4. It is observed that some water points show a stoichiometric distribution of Na^+ ions with Cl^- ions, indicating the common sodium chloride (halite) origin of these two chemical elements. However, other water points show a relative excess or deficit in sodium levels relative to slope1 (halite dissolution), which can be explained by the existence of base exchange phenomena that varied the concentration of sodium relative to that of chloride. The phenomenon of cation exchange is highlighted in other aquifers in the Algerian Sahara [Belaksier et al. 2016].
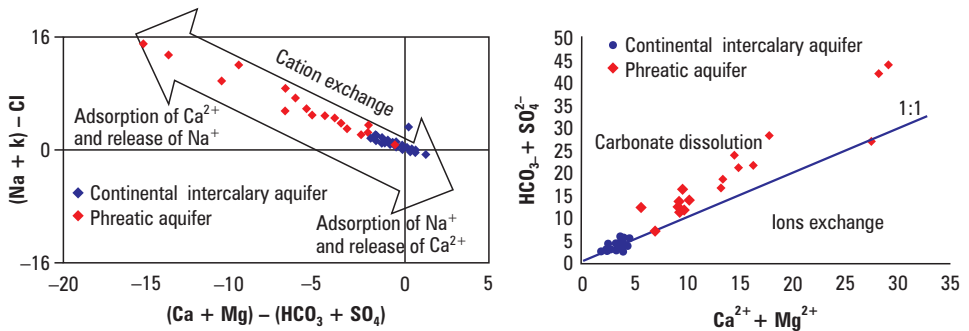
Source: Authors' own study

**Fig. 5.** Ion exchange in the phreatic and intercalary aquifer in the El Golea zone

4.2. Hierarchical clustering (HCA)

Figure 6 shows the hierarchical clustering dendrogram of the water samples in the study area. It shows two main groups. The first group is composed of highly mineralized groundwater taken from the phreatic aquifer (P5, P10, P18 and P20), while the second group includes the rest of the moderately mineralized waters of the unconfined aquifer and the groundwater of the intercalary continent with low mineralization (f1 to f39). The first group consists of samples taken from wells located near the salt lake (Garaa). They are characterized by a very high electrical conductivity ranging from

2440 μS/cm to 6070 μs/cm and an average TDS > 3000 mg/l. The second group consists of two subgroups, connected at a distance of 2400 steps.

The first one includes very similar samples formed by groundwater. They are less gathered than the second subgroup, characterized by an average EC reaching 1400 μS/cm and an average TDS of 1080 mg/l, the quality of the water decreasing from right to left. The third subgroup includes the rest of the boreholes capturing the CI groundwater (f1 to f39) of good quality water, which has an average electrical conductivity equal of 450 μS/cm and an average TDS of 274 mg/l, mineral waters sold on the internal market since 1996.
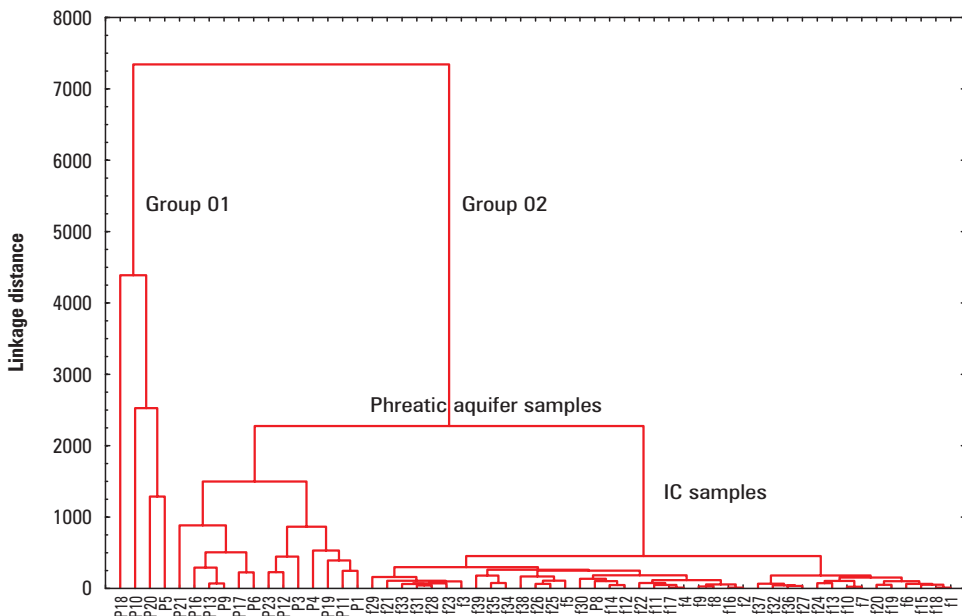
Source: Authors' own study

**Fig. 6.** Hierarchical ascending classification of samples water in the El Golea region

4.3. Principal component analysis

The correlation matrix shows that the strong correlations between most of the variables are positive, i.e. their concentrations move in the same direction. Ca^{2+} is strongly correlated with HCO_3^-, SO_4^{2-}, EC and TDS and Mg^{2+} is strongly correlated with SO_4^{2-}, EC and TDS, indicating that these elements are related and/or have the same origin (Leaching of evaporitic formations, $CaSO_4$ gypsum, $MgSO_4$ mirabilite and dissolution of carbonate formations ($Ca(HCO_3)_2$ limestone, and $Mg(HCO_3)_2$ dolomite). The strong correlations between the saliferous ions Na^+, Mg^{2+} and Cl^- characterizing the groundwater show the strong influence of the Sabkha (El-Garaa salt lake).

Table 1. Correlation matrix coefficients between the physico-chemical parameters in the water of the phreatic and the Continental Intercalary aquifers

	EC	TDS	Ca^{2+}	Mg^{2+}	Na^+	K^+	HCO_3^-	SO_4^{2-}	Cl^-	NO_3^-	pH	T
EC	1.000											
TDS	0.989	1.000										
Ca^{2+}	0.808	0.839	1.000									
Mg^{2+}	0.903	0.897	0.659	1.000								
Na^+	0.940	0.945	0.855	0.843	1.000							
K^+	0.763	0.803	0.720	0.726	0.816	1.000						
HCO_3^-	0.669	0.720	0.852	0.611	0.827	0.735	1.000					
SO_4^{2-}	0.982	0.976	0.845	0.891	0.924	0.737	0.659	1.000				
Cl^-	0.941	0.937	0.744	0.918	0.952	0.831	0.693	0.909	1.000			
NO_3^-	−0.361	−0.400	−0.420	−0.372	−0.398	−0.352	−0.542	−0.360	−0.280	1.000		
pH	0.398	0.380	0.514	0.429	0.454	0.346	0.536	0.413	0.386	−0.120	1.000	
T	−0.055	−0.056	0.009	−0.071	−0.049	−0.256	−0.023	−0.072	−0.034	0.090	−0.003	1.000

First we must select the number of factorial axes that we want to keep. For this purpose we will follow its rules; in normalized CPA; we are only interested in the axes with an eigenvalues greater than 1 [Kaiser 1958]. The first axes is selected in order to reach a certain percentage of explained inertia (> 5%) "minimum inertia rule". Figure 7 presents a decreasing curve of the percentage of all factors, which as a graphical representation also allows to discern the number of factors needed for a better visualization of the results:
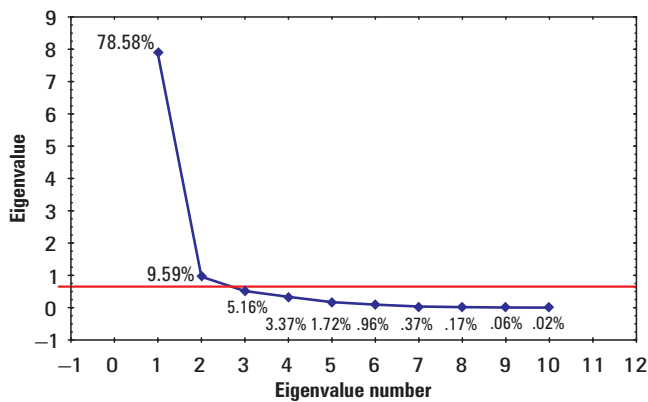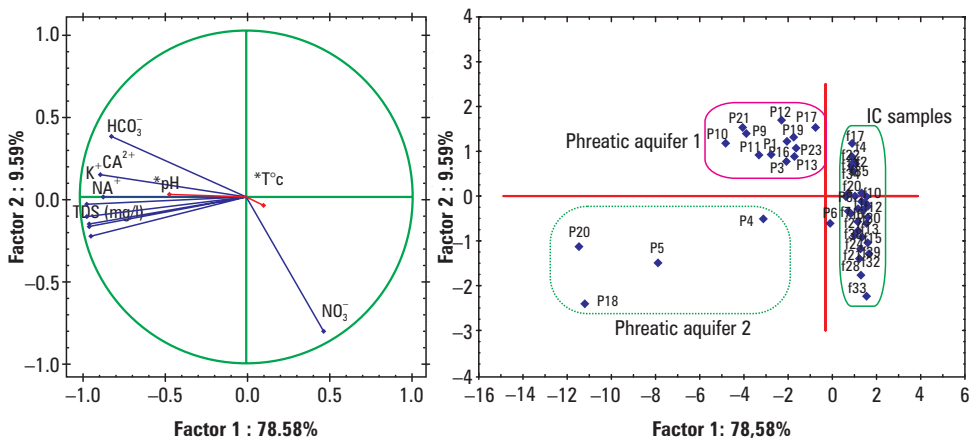

Source: Authors' own study

Fig. 7. Eigenvalues of correlation matrix

In Figure 7 the calculation has been stopped at two axes, axes F1 and F2.

Principal component analysis (PCA) was performed to support the relationships between the main chemical elements (Cl^-, Na^+, K^+, Ca^{2+}, Mg^{2+}, SO_4^{2-}, HCO_3^-, and NO_3^-) and physical parameters (pH, T and electrical conductivity). The results of the PCA are presented in the Figure 8. In the analysis, two principal components were considered, representing 88.17% of the total variance. This indicates an unbounded structuring of the variance, as the water chemistry is conditioned by various factors. Axis 1 expresses (78.58%) of the variance and opposes the main elements to nitrate. It explains the different origins of these ions. These axes reflect the role of the mixture of the dissolution of minerals (halite, gypsum and / or anhydrite, limestone and/or dolomite) and the influence of the saline waters of the Sabkha on the variation of the groundwater chemistry. The approved evolution of Ca^{2+} in parallel with (HCO_3^-) and the complete alkalinity of factor 1 indicate that the increase of Ca^{2+} content in groundwater is associated with the processes of gypsum dissolution and carbonate alteration. The results of the statistical units in the I–II factorial design, shown in the Figure 8, indicate a progressive geochemical evolution from top to bottom. In addition, this statistical method suggests that any mixing relationship cannot be explained by a simple two-component mixture between groundwater and CI groundwater.

Source: Authors' own study

Fig. 8. Projection of the variables and cases on the factor plane (1–2)

Several possible groundwater compositions can be identified. One endpoint is represented by highly mineralized waters with high TDS levels, mixed with Na–Mg from the influence of salt water and soil leaching from irrigation return flows. The high concentrations of chlorides in these waters show that the increase in salinity is mainly influenced by the dissolution of the salt formations and/or the influence of the Garaa waters. The second endpoint is represented by groundwater with medium mineraliza-

tion and a very variable TDS, explained by the presence of surface or natural pollution resulting from the contact between the groundwater and the reservoir rock.

- The third one is characterized by low contents of major ions and especially chlorides and sulphates explained by the influence of the Sabkha waters and the return of irrigation water.
- The study of the second factor (9.59% of the variance) suggests a third water element represented by waters with high concentration due to recent waters of meteoric origin.
- The results provided by the PCA and the hierarchical clustering (HAC) are in perfect agreement. The transition from one geochemical facies to another and the variation in the geochemical characteristics of the groundwater in the El Golea region reflect the complexity of the hydrogeochemical processes that lead to the mineralization of the water in this area.

5. Isotopic study

The first isotope studies in the IC are based on [Gonfiantini et al. 1974]. These studies confirm that isotopic methods are very important for assessing the flow in the Northern Sahara aquifer system and give an idea of the age of the water stored in the CI and the phreatic aquifer.

This was partially resolved by [Moulla et al. 2012], who published a large geochemical and isotopic database for the CI in the GWE (Great Western Erg) sub-basin, giving a "broad" picture on the hydrogeology and hydrochemistry of the aquifer in our region. Our work here retraced the continuity with previous studies [Darling et al. 2018, Fenazi et al. 2022], focusing on a small part of the GWE. The study is based on a comprehensive set of hydrochemical and isotopic data on the waters of the intercalary continental and the phreatic aquifers of El Golea, and compares them to the results of previous studies. Stable oxygen and hydrogen isotopes are generally considered to be conservatively transported in shallow aquifers [Kim et al. 2003]. The use of $\delta18O$ and $\delta2H$ isotopes in hydrogeology provides information on the origin and movement of groundwater [Boucenna et al. 2018]. It can provide an assessment of physical processes affecting water bodies, such as evaporation and mixing [Wolfgang and Mebus Geyh 2000]. The local meteoric water line is defined by the equation [Abid et al. 2009]:

$$\delta2H = 8 \cdot \delta18O + 13.$$

The average isotopic composition of the groundwater is close to the isotopic composition of modern rainfall in the Sahara. This indicates the presence of a mixture of current precipitation and ancient water from the deep aquifer that reached the open aquifer through the return of irrigation water.

The $\delta2H$–$\delta18O$ diagram shows that all points representing CI and Ph, aquifer groundwaters are situated below the GMWL, the samples are divided into three groups. In the first group, the formation of the shallow aquifer (Barremian sand) and the

areas in the proximity of the recharge surfaces induce a "rejuvenation" of these waters [Darling et al. 2006]. The second group is characterized by the waters of the phreatic aquifer, which have an isotopic composition similar to that of the CI, explaining the existence of fissured or semi-permeable horizons between the two superimposed aquifers, allowing vertical exchanges between them. The points collected in the Continental Intercalary aquifer with low isotopic contents may correspond to the most confined part of the deep aquifer. The values of these contents are relatively low in the basal sandstone formations of the Continental Intercalary.
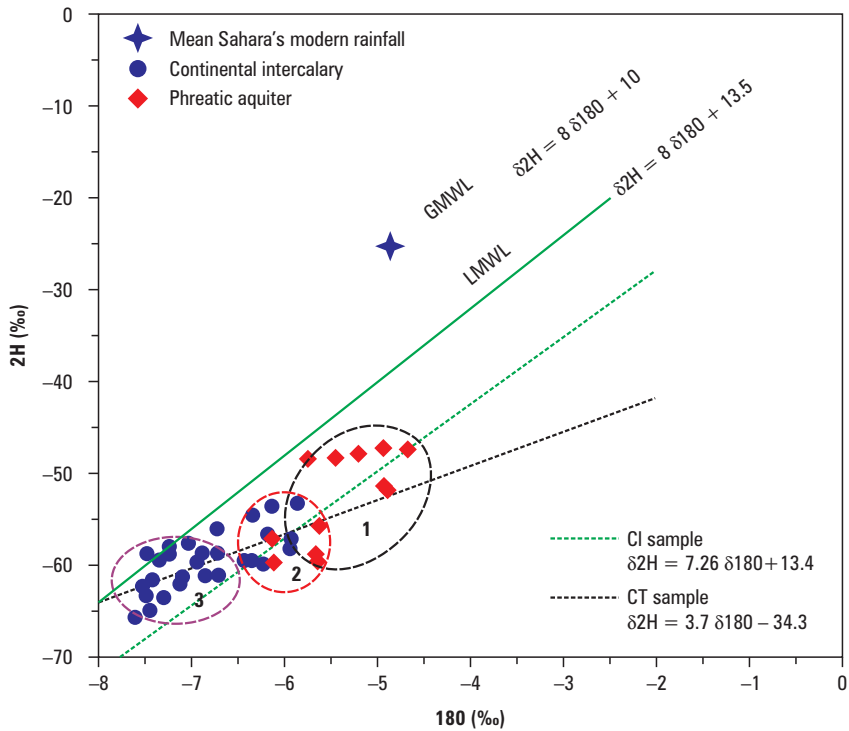
Source: Authors' own study

Fig. 9. The meteoric water line of the El Golea region

6. Conclusion

The application of statistical, hydrogeochemical and isotopic approaches provides information on the hydrogeochemistry of the groundwater and assesses the water quality in the hyper-arid region of El Golea in southern Algeria. The conclusions are the following:

The bivariate statistical analysis and the correlation matrix show a strong positive correlation between the different chemical ions (Ca^{2+}, Mg^{2+}, Na^+, HCO_3 and SO_4^{2-}). The

high content of Cl^-, SO_4^{2-} and NO_3^- anions in the unconfined aquifer indicate a high level of groundwater pollution. The (Ca^{2+} + Mg^{2+}) and (HCO_3^- + SO_4^{2-}) plots indicate the dominance of direct ion exchange especially in the clay sediments. The dominance of the direct ion exchange between Na^+ and Ca^{2+}, Mg^{2+}, supports the increasing Na^+ content in the two aquifers. Calcite precipitation and dolomite dissolution cause the dolomitization process in the study area. The high correlation between TDS and Cl^-, SO_4^{2-}, and Na^+ strongly supports the impact of agricultural activities on groundwater quality.

The geochemical data confirm the water-rock interaction (dissolution of calcite, dolomite, and dissolution of gypsum, precipitation of $CaCO_3$ and rock dolomitization), which takes place in the study area.

Principal component analysis allowed the extraction of a two-factor. The strong positive charge of F1 (EC, TDS, Na^+, K^+, Ca^{2+}, Mg^{2+}, Cl^-, and SO_4^{2-}) represents carbonate weathering, silicate dissolution and ion exchange processes; F2 (NO_3) indicates the contribution of soil CO_2 and the impact of anthropogenic activities. The phreatic aquifer water that reaches the saturated zone is a "mixture" of water that infiltrates directly and water stored in the soil during major rainfall events. This situation is explained by the presence of mixed water with a high isotopic content in the proximity of the recharge areas. In the CI aquifer, the water is older and has a more homogeneous and lower isotopic composition.

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