Dear Professor Giudici,

thank you very much for your comments and suggestions. We modified our manuscript to show how it can be of interest to an international audience:

- the aquifers studied are important both quantitatively and as a scarce resource in a semi-arid to hyper-arid environment; there are very few studies on these aquifers;

- inverse modeling is used to quantitatively assess the modifications of the chemical composition of water along the flowpath combining mass transfer between aquifers and water and reactive mixing; isotope data are used to discriminate statistically equivalent models;

- the methodology and data can be integrated in a straightforward manner in a general framework where geochemical models (PhreeqC or others), crop models and land use models are operationally interfaced, as the achievement of cooperative efforts during the last decades referred to at the end of the introduction.

Modifications are not limited to the introduction and are shown by correction marks in the margins throughout the manuscript.

With our best regards,

Pr. Guilhem Bourri and Dr Rabia Slimani
Identification of dominant hydrogeochemical processes for groundwaters in Algerian Sahara supported by inverse modeling of chemical and isotopic data

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Abstract

Unpublished chemical and isotopic data taken in November 1992 from the three major Saharan aquifers namely, the “Continental Intercalaire” (CI), the “Complexe Terminal” (CT) and the Phreatic aquifer (Phr) were integrated with original samples in order to chemically and isotopically characterize the largest Saharan aquifer system and investigate the processes through which groundwaters acquire their mineralization. Instead of classical Debye-Hückel extended law, Specific Interaction Theory (SIT) model, recently incorporated in Phreeqc 3.0 was used. Inverse modeling of hydrochemical data constrained by isotopic data was used here to quantitatively assess the influence of geochemical processes: at depth, the dissolution of salts from the geological formations during upward leakage without evaporation explains the transitions from CI to CT and to a first end member, cluster of Phr (cluster I); near the surface, the dissolution of salts from sebkhas by rainwater explains another cluster of Phr (cluster II). In every case, secondary precipitation of calcite occurs during dissolution. All Phr waters result from the mixing of these two clusters together with calcite precipitation and ion exchange processes. These processes are quantitatively assessed by Phreeqc model. Globally, gypsum dissolution and calcite precipitation were found to act as a carbon sink.

Keywords: hydrochemistry, stable isotopes, Sahara, Algeria

1. INTRODUCTION

A scientific study published in 2008 (OECD, 2008) showed that 85% of the world population lives in the driest half of the earth. More than 1 billion people residing in arid and semi-arid areas of the world have access to only few or non-renewable water resources. The North-Western Sahara Aquifer System (NWSAS) is one of the largest captive reservoirs in the world and its huge water reserves are essentially composed of an old component. It is represented by two main deep aquifers, the Continental Intercalaire and the Complexe Terminal. This system covers
a surface area of more than one million km$^2$ of which 700,000 km$^2$ are in Algeria, 80,000 km$^2$

in Tunisia and 250,000 km$^2$ in Libya. With regard to the climatic conditions of the Sahara, these formations are poorly renewed: about 1 billion m$^3$/year essentially infiltrated in the Piedmont of the Saharan Atlas in Algeria, as well as in the Dahar and Djebel Nafusa in Tunisia and Libya respectively. However, the very large expansion of the system as well as the great thickness of the aquifer layers has favored the accumulation of huge water reserves. Ouargla basin occurs right in the middle of the NWSAS and thus benefits from its Groundwater resources (Fig. 1) are contained in three main reservoirs (UNESCO, 1972; Eckstein and Eckstein, 2003; OSS, 2003, 2008). These are namely:

- at the top, the phreatic aquifer (Phr), in the Quaternary sandy gypsum permeable formations of Quaternary, is almost unexploited, due to its extreme salinity (50 g/L);
- in the middle, the “Complexe Terminal” (CT) (Cornet and Gouscov, 1952; UNESCO, 1972) is the most exploited and includes several aquifers in different geological formations. Groundwater circulates in one or the two lithostratigraphic formations of the Eocene and Senonian carbonates or in the Mio-pliocene sands;
- at the bottom, the “Continental Intercalaire” (CI), hosted in the lower Cretaceous continental formations (Barremian and Albian), mainly composed of sandstones, sands and clays. It is only partially exploited because of its significant depth.

The integrated management of these groundwaters is presently a serious issue for local water resources managers due to the large extension of the aquifers and the complexity of the relations between them. Several studies (Guendouz, 1985; Fontes et al., 1986; Guendouz and Moulla, 1996; Edmunds et al., 2003; Guendouz et al., 2003; Hamdi-Aïssa et al., 2004; Foster et al., 2006; OSS, 2008) started from chemical and isotopic information ($^2$H, $^{18}$O, $^{234}$U, $^{238}$U, $^{36}$Cl) to characterize the relationships between aquifers. In particular, such studies focused on the recharge of the deep CI aquifer system. These investigations especially dealt with water chemical facies, mapped isocontents of various parameters, and reported typical geochemical ratios ([SO$_4^{2-}$]/[Cl$^-$], [Mg$^{2+}$]/[Ca$^{2+}$]) as well as other correlations. Minerals / solutions equilibria were checked by computing saturation indices with respect to calcite, gypsum, anhydrite and halite, but processes were only qualitatively assessed.

The present study aims at applying for the first time ever in Algeria, inverse modeling to an extreme environment, featured by a lack of data on a scarce natural resource (groundwater). New data were hence collected in order to characterize the hydrochemical and the isotopic composition of the major aquifers in the Saharan region of Ouargla. New possibilities offered by progress in geochemical modeling were used. The objective was also to identify the origin of the mineralization and the water-rock interactions that occur along the flowpath. More specifically, inverse modeling of chemical reactions allows one to select the best conceptual model for the interpretation of the geochemical evolution of Ouargla aquifer system. The stepwise inversion strategy involves designing a list of scenarios (hypotheses) that take into consideration the most plausible combinations of geochemical processes that may occur within the studied medium. After resolving the scenarios in a stepwise manner, the one that provides the best conceptual geochemical model is then selected, which allowed (Dai et al., 2006) to optimize simultaneously transmissivities and geochemical transformations in a confined aquifer. Inverse modeling with Phreeqc 3.0 was used here in a different way, only on geochemical data but for several aquifers, to account for the modifications of the composition of water along the flowpath. At least two chemical analyses
of groundwater at different points of the flow path, and a set of phases (minerals and/or gases) which potentially react while water circulates are needed to operate the program (Charlton et al., 1996).

A number of assumptions are inherent to the application of inverse geochemical modeling: (i) the two groundwater analyses from the initial and the final boreholes should represent groundwater that flows along the same flow path, (ii) dispersion and diffusion do not significantly affect groundwater chemistry, (iii) a chemical steady-state prevails in the groundwater system during the time considered, and (iv) the mineral phases used in the inverse calculation are or were present in the aquifer (Zhu and Anderson, 2002). The soundness or the validity of the results depends on a valid conceptualization of the groundwater system, on the validity of the basic hydrogeochemical concepts and principles, and on the accuracy of model input data, and the level of understanding of the geochemical processes occurring in the area (Güler and Thyne, 2004; Sharif et al., 2008).

These requirements are fulfilled in the region of Ouargla, which can be considered as a “window” open on the largest Saharan aquifer, and thus one of the largest aquifers in the world in a semi-arid to hyper-arid region subject to both global changes: urban sprawl and climate change. The methodology developed here and the data collected can easily be integrated in the PRECOS framework proposed for the management of environmental resources (Trolard et al., 2016).

2. METHODOLOGY

2.1. Presentation of the study area

The study area is located in the northeastern desert of Algeria “Lower-Sahara” (Le Houérou, 2009) near the city of Ouargla (Fig. 1), 31°54’ to 32°1’ N and 5°15’ to 5°27’ E, with a mean elevation of 134 m a.s.l.). It is located in the quaternary valley of Oued Mya basin. Present climate belongs to the arid Mediterranean-type (Dubief, 1963; Le Houérou, 2009; ONM, 1975/2013), as it is characterized by a mean annual temperature of 22.5 °C, a yearly rainfall of 43.6 mm/yr and a very high evaporation rate of 2,138 mm/yr.

Ouargla’s region and the entire Lower Sahara has experienced during its long geological history alternating marine and continental sedimentation phases. During Secondary era, vertical movements affected the Precambrian basement causing in particular collapse of its central part, along an axis passing approximately through the Oued Righ valley and the upper portion of the valley oued Mya. According to Furon (1960), a epicontinental sea spread to the Lower Eocene of northern Sahara. After the Oligocene, the sea gradually withdrew. It is estimated at present that this sea did not reach Ouargla and transgression stopped at the edge of the bowl (Furon, 1960; LeLièvre, 1969). The basin is carved into Mio-pliocene (MP) deposits, which alternate with red sands, clays and sometimes marls; gypsum is not abundant and dated from Pontian (MP) (Cornet and Gouscov, 1952; Dubief, 1953; Ould Baba Sy and Besbes, 2006). The continental Pliocene consists of a local limestone crust with puddingstone or lacustrine limestone (Fig. 2), shaped by eolian erosion into flat areas (regs). The Quaternary formations are lithologically composed of alternating layers of permeable sand and relatively impermeable marl (Aumassip et al., 1972; Chellat et al., 2014).

The exploitation of Mio-pliocene aquifer is ancient and at the origin of the creation of the oasis (LeLièvre, 1969; Moulias, 1927). The piezometric level was higher (145 m a.s.l.) but over-exploitation at the end of the XIXth century led to a catastrophic decrease of the resource, with presently more than 900 boreholes (ANRH, 2011).
The exploitation of Senonian aquifer dates back to 1953 at a depth between 140 to 200 m, with a small initial rate of ca. 9 L s\(^{-1}\); two boreholes have been exploited since 1965 and 1969, with a total flowrate of ca. 42 L s\(^{-1}\), for drinking water and irrigation.

The exploitation of Albian aquifer dates back to 1956, presently, two boreholes are exploited:

- El Hedeb I, 1,335 m deep, with a flowrate of 141 L s\(^{-1}\);
- El Hedeb II, 1,400 m deep, with a flowrate of 68 L s\(^{-1}\).

### 2.2. Sampling and analytical methods

The sampling programme consisted of collecting samples along transects corresponding to directions of flow for both Phr and CT aquifers while it was possible to collect only eight samples from the CI. A total of 107 samples were collected during a field campaign in 2013, along the main flowpath of Oued Mya. 67 of them were from piezometers tapping the phreatic aquifer, 32 from CT wells and the last 8 from boreholes tapping the CI aquifer (Fig. 3). Analyses of Na\(^+\), K\(^+\), Ca\(^{2+}\), Mg\(^{2+}\), Cl\(^-\), SO\(_4\)^{2-}\) and HCO\(_3\)^- were performed by ion chromatography at Algiers Nuclear Research Center (CRNA). Previous and yet unpublished data (Guendouz and Moulla, 1996) sampled in 1992 are used here too: 59 samples for Phr aquifer, 15 samples for CT aquifer and 3 samples for the CI aquifer for chemical analyses, data \(^{18}\)O and \(^{3}\)H (Guendouz and Moulla, 1996).

### 2.3. Geochemical method

Phreeqc was used to check minerals / solution equilibria using the specific interaction theory (SIT), i.e. the extension of Debye-Hückel law by Scatchard and Guggenheim incorporated recently in Phreeqc 3.0 (Parkhurst and Appelo, 2013). Inverse modeling was used to calculate the number of minerals and gases’ moles that must respectively dissolve or precipitate/degas to account for the difference in composition between initial and final water end members (Plummer and Back, 1980; Kenoyer and Bowser, 1992; Deutsch, 1997; Plummer and Sprinkle, 2001; Güler and Thyne, 2004; Parkhurst and Appelo, 2013). This mass balance technique has been used to quantify reactions controlling water chemistry along flow paths (Thomas et al., 1989). It is also used to quantify the mixing proportions of end-member components in a flow system (Kuells et al., 2000; Belkhiri et al., 2010, 2012).

Inverse modeling involves designing a list of scenarios (modelling setups) that take into account the most plausible combinations of geochemical processes that are likely to occur in our system. For example, the way to identify whether calcite dissolution/precipitation is relevant or not consists of solving the inverse problem under two alternate scenarios: (1) considering a geochemical system in which calcite is present, and (2) considering a geochemical system without calcite. After simulating the two scenarios, it is usually possible to select the setup that gives the best results as the solution to the inverse modeling according to the fit between the modeled and observed values. Then one can conclude whether calcite dissolution/precipitation is relevant or not. This stepwise strategy allows us to identify the relevance of a given chemical process by inversely solving the problem through alternate scenarios in which the process is either participating or not (Dai et al., 2006).

In geochemical modeling inverse, soundness of results are dependent upon valid conceptualization of the system, validity of basic concepts and principles, accuracy of input data, and level of understanding of the geochemical processes. We use the information from the lithology, general hydrochemical evolution patterns, saturation indices and mineral stability diagrams to constrain the inverse models.
3. RESULTS AND DISCUSSION

Tables 1 to 4 illustrate the results of the chemical and the isotopic analyses. Samples are ordered according to an increasing electric conductivity (EC), and this is assumed to provide an ordering for increasing salt content. In both phreatic and CT aquifers, temperature is close to 25°C, while for CI aquifer, temperature is close to 50°C. The values presented in tables 1 to 5 are raw analytical data that were corrected for defects of charge balance before computing activities with Phreeqc. As analytical errors could not be ascribed to a specific analyte, the correction was made proportionally. The corrections do not affect the anions to anions mole ratios such as for $\frac{[\text{HCO}_3^-]}{([\text{Cl}^-]+2[\text{SO}_4^{2-}])}$ or $\frac{[\text{SO}_4^{2-}]}{[\text{Cl}^-]}$, whereas they affect the cation to anion ratio such as for $[\text{Na}^+]/[\text{Cl}^-]$.

3.1. Characterization of chemical facies of the groundwater

Piper diagrams drawn for the studied groundwaters (Fig. 4) broadly show a scatter plot dominated by a Chloride-Sodium facies. However, when going into small details, the widespread chemical facies of the Phr aquifer is closer to the NaCl cluster than those of CI and CT aquifers. Respectively, CaSO$_4$, Na$_2$SO$_4$, MgSO$_4$ and NaCl are the most dominant chemical species (minerals) that are present in the phreatic waters. This sequential order of solutes is comparable to that of other groundwater occurring in North Africa, and especially in the neighboring area of the chotts (depressions where salts concentrate by evaporation) Merouane and Melhir (Vallès et al., 1997; Hamdi-Aïssa et al., 2004).

3.2. Spatial distribution of the mineralization

The salinity of the phreatic aquifer varies considerably depending on the location (namely, the distance from wells or drains) and time (due to the influence of irrigation) (Fig. 5a). Its salinity is low around irrigated and fairly well-drained areas, such as the palm groves of Hassi Miloud, just north of Ouargla (Fig. 3) that benefit from freshwater and are drained to the sebkha Oum el Raneb. However, the three lowest salinity values are observed in the wells of Ouargla palm-grove itself, where the Phr aquifer watertable is deeper than 2 m. Conversely, the highest salinity waters are found in wells drilled in the chotts and sebkhas (a sebkha is the central part of a chott where salinity is the largest) (Safioune and Oum er Raneb) where the aquifer is often shallower than 50 cm. The salinity of the CT (Mio-pliocene) aquifer (Fig. 5b) is much lower than that of the Phr aquifer, and ranges from 1 to 2 g/L; however, its hardness is larger and it contains more sulfate, chloride and sodium than the waters of the Senonian formations and those of the CI aquifer. The salinity of the Senonian aquifer ranges from 1.1 to 1.7 g/L, while the average salinity of the CI aquifer is 0.7 g/L (Fig. 5c).

A likely contamination of the Mio-pliocene aquifer by phreatic groundwaters through casing leakage in an area where water is heavily loaded with salt and therefore particularly aggressive cannot be excluded.

3.3. Saturation Indices

The calculated saturation indices (SI) reveal that waters from CI at 50°C are close to equilibrium with respect to calcite, except for 3 samples that are slightly oversaturated. They are however all undersaturated with respect to gypsum (Fig. 6). Moreover, they are oversaturated with respect to dolomite and undersaturated with respect to anhydrite and halite (Fig. 7).
Waters from CT and phreatic aquifers show the same pattern, but some of them are more largely oversaturated with respect to calcite, at 25 °C. However, several phreatic waters (P031, P566, PLX4, PL18, P002, P023, P116, P066, P162 and P036) that are located in the sebkhas of Sefioune, Oum-er-Raneb, Bamendil and Ain el Beida’s chott are saturated with gypsum and anhydrite. This is in accordance with highly evaporative environments found elsewhere (UNESCO, 1972; Hamdi-Aïssa et al., 2004; Slimani, 2006).

No significant trend of SI from south to north upstream and downstream of Oued Mya (Fig. 7) is observed. This suggests that the acquisition of mineralization is due to geochemical processes that have already reached equilibrium or steady state in the upstream areas of Ouargla.

3.4. Change of facies from the carbonated cluster to the evaporites’ cluster

The facies shifts progressively from the carbonated (CI and CT aquifers) to the evaporites’ one (Phr aquifer) with an increase in sulfates and chlorides at the expense of carbonates (SI of gypsum, anhydrite and halite). This is illustrated by a decrease of the \([\text{HCO}_3^-]/(\text{[Cl]} + 2\text{[SO}_4^{2-}])\) ratio (Fig. 8) from 0.2 to 0 and of the \([\text{SO}_4^{2-}]/\text{[Cl]}\) ratio from 0.8 to values smaller than 0.3 (Fig. 9) while salinity increases. Carbonate concentrations tend towards very small values, while it is not the case for sulfates. This is due to both gypsum dissolution and calcite precipitation. Chlorides in groundwater may come from three different sources: (i) ancient sea water entrapped in sediments; (ii) dissolution of halite and related minerals that are present in evaporite deposits and (iii) dissolution of dry fallout from the atmosphere, particularly in these arid regions (Matiatos et al., 2014; Hadj-Ammar et al., 2014).

\([\text{Na}^+]/\text{[Cl]}\) ratio ranges from 0.85 to 1.26 for CI aquifer, from 0.40 to 1.02 for the CT aquifer, from 0.13 to 2.15 for the Phr aquifer. The measured points from the three considered aquifers are linearly scattered with good approximation around the unity slope straight line that stands for halite dissolution (Fig. 10). The latter appears as the most dominant reaction occurring in the medium. However, at very high salinity, \(\text{Na}^+\) seems to swerve from the straight line, towards smaller values.

A further scrutiny of Fig. 10 shows that CI waters are very close to the 1:1 line. CT waters are enriched in both \(\text{Na}^+\) and \(\text{Cl}^-\) but slightly lower than the 1:1 line while phreatic waters are largely enriched and much more scattered. CT waters are closer to the seawater mole ratio (0.858), but some lower values imply a contribution from another source of chloride than halite or from entrapped seawater. Conversely, a \([\text{Na}^+]/\text{[Cl]}\) ratio larger than 1 is observed for phreatic waters, which implies the contribution of another source of sodium, most likely sodium sulfate, that is present as mirabilite or thenardite in the chotts and the sebkhas areas.

\([\text{Br}^-]/\text{[Cl]}\) ratio ranges from \(2 \times 10^{-3}\) to \(3 \times 10^{-3}\). The value of this molar ratio for halite is around 2.5 \(10^{-3}\), which matches the aforementioned range and confirms that halite dissolution is the most dominant reaction taking place in the studied medium.

In the CI, CT and Phr aquifers, calcium originates both from carbonate and sulfate (Fig. 11 and 12). Three samples from CI aquifer are close to the \([\text{Ca}^{2+}]/[\text{HCO}_3^-] 1:2\) line, while calcium sulfate dissolution explains the excess of calcium. However, nine samples from Phr aquifer are depleted in calcium, and plot under the \([\text{Ca}^{2+}]/[\text{HCO}_3^-] 1:2\) line. This cannot be explained by precipitation of calcite, as some are undersaturated with respect to that mineral, while others are oversaturated.

In this case, a cation exchange process seems to occur and lead to a preferential adsorption of divalent cations, with a release of \(\text{Na}^+\). This is confirmed by the inverse modeling that is developed below and which implies \(\text{Mg}^{2+}\) fixation and \(\text{Na}^+\) and \(\text{K}^+\) releases.
Larger sulfate values observed in the phreatic aquifer (Fig. 12) with \([\text{Ca}^{2+}]/[\text{SO}_4^{2-}] < 1\) can be attributed to a Na-Mg sulfate dissolution from a mineral bearing such elements. This is for instance the case of bloedite.

3.5. Isotope geochemistry

CT and CI aquifer exhibit depleted and homogeneous \(^{18}\text{O}\) contents, ranging from \(-8.32\%\) to \(-7.85\%\). This was already previously reported by many authors (Edmunds et al., 2003; Guendouz et al., 2003; Moulla et al., 2012). On the other hand, \(^{18}\text{O}\) values for the phreatic aquifer are widely dispersed and vary between \(-8.84\%\) to \(3.42\%\) (Table 5). Waters located north of the virtual line connecting approximately Hassi Miloud to sebkhet Safioune, are found more enriched in heavy isotopes and are thus more evaporated. In that area, water table is close to the surface and mixing of both CI and CT groundwaters with phreatic ones through irrigation is nonexistent. Conversely, waters located south of Hassi Miloud up to Ouargla city show depleted values. This is the clear fingerprint of a contribution to the Phr waters from the underlying CI and CT aquifers (Gonfiantini et al., 1975; Guendouz, 1985; Fontes et al., 1986; Guendouz and Moulla, 1996).

Phreatic waters result from a mixing of two end-members. An evidence for this is given by considering the \([\text{Cl}^-], \ ^{18}\text{O}\) relationship (Fig. 13). The two clusters are: i) a first cluster of \(^{18}\text{O}\) depleted groundwater (Fig. 14), and ii) another cluster of \(^{18}\text{O}\) enriched groundwater with positive values and a high salinity. The latter is composed of phreatic waters occurring in the northern part of the study region.

Cluster I represents the waters from CI and CT whose isotopic composition is depleted in \(^{18}\text{O}\) (average value around \(-8.2\%\)) (Fig. 13). They correspond to an old water recharge (paleorecharge); whose age estimated by means of \(^{14}\text{C}\), exceeds 15,000 years BP (Guendouz, 1985; Guendouz and Michelot, 2006). So, it is not a water body that is recharged by recent precipitation. It consists of CI and CT groundwaters and partly of phreatic waters, and can be ascribed to an upward leakage favored by the extension of faults near Amguid El-Biod dorsal.

Cluster II, observed in Sebkhet Safioune, can be ascribed to the direct dissolution of surficial evaporitic deposits conveyed by evaporated rainwater.

Evaporation alone cannot explain the distribution of data that is observed (Fig. 13). An evidence for this is given in a semi-logarithmic plot (Fig. 14), as classically obtained according to the simple approximation of Rayleigh equation (cf. Appendix):

\[
\delta^{18}\text{O} = 1000 \times (1 - \alpha) \log [\text{Cl}^-] + k, \quad \text{(1)}
\]

\[
\approx -\epsilon \log [\text{Cl}^-] + k, \quad \text{(2)}
\]

where \(\alpha\) is the fractionation factor during evaporation, \(\epsilon \equiv -1000 \times (1 - \alpha)\) is the enrichment factor and \(k\) is a constant (Ma et al., 2010; Chkir et al., 2009). CI and CT waters are better separated in the semi-logarithmic plot because they are differentiated by their chloride content. According to equation (1), simple evaporation gives a straight line (solid line in Fig. 14). The value of \(\epsilon\) used is the value at 25°C, which is equal to \(-73.5\).

P115 is the only sample that appears on the straight evaporation line (Fig. 14). It should be considered as an outlier since the rest of the samples are all well aligned on the logarithmic fit derived from the mixing line of Figure 13.
The phreatic waters that are close to cluster I (Fig. 13) correspond to groundwaters occurring in the edges of the basin (Hassi Miloud, piezometer P433) (Fig. 14). They are low-mineralized and acquire their salinity via two processes, namely: dissolution of evaporites along their underground transit up to Sebkhet Safioune and dilution through upward leakage by the less-mineralized waters of CI and CT aquifers (for example Hedeb I for CI and D7F4 for CT) (Fig. 14) (Guendouz, 1985; Guendouz and Moulla, 1996).

The rates of the mixing that are due to upward leakage from CI to CT towards the phreatic aquifer can be calculated by means of a mass balance equation. It only requires knowing the $\delta$ values of each fraction that is involved in the mixing process.

The $\delta$ value of the mixture is given by:

$$\delta_{\text{mix}} = f \times \delta_1 + (1 - f) \times \delta_2$$  \hspace{1cm} (3)

where $f$ is the fraction of CI aquifer, $1 - f$ the fraction of the CT and $\delta_1$, $\delta_2$ are the respective isotope contents.

Average values of mixing fractions from each aquifer to the phreatic waters computed by means of equation (3) gave the rates of 65% for CI aquifer and 35% for CT aquifer.

A mixture of a phreatic water component that is close to cluster I (i.e. P433) with another component which is rather close to cluster II (i.e. P039) (Fig. 13 and 14), for an intermediate water with a $\delta^{18}O$ signature ranging from $-5\%$ to $-2\%$ gives mixture fraction values of 52% for cluster I and 48% for cluster II. Isotope results will be used to independently cross-check the validity of the mixing fractions derived from an inverse modeling involving chemical data (see section 3.6).

Turonian evaporites are found to lie in between CI deep aquifer and the Senonian and Miocene formations bearing CT aquifer. CT waters can thus simply originate from ascending CI waters that dissolve Turonian evaporites, a process which does not involve any change in $^{18}O$ content.

Conversely, phreatic waters result to a minor degree from evaporation and mostly from dissolution of sebkhas evaporites by $^{18}O$ enriched rainwater and mixing with CI-CT waters.

### 3.5.1. Tritium content of water

Tritium contents of Phr aquifer are relatively small (Table 5), they vary between 0 and 8 TU. Piezometers PZ12, P036 and P068 show values close to 8 TU, piezometers P018, P019, P416, P034, P042 and P093 exhibit values ranging between 5 and 6 TU, and the rest of the samples’ concentrations are lower than 2 TU.

These values are dated back to November 1992 so they are old values and they are considered high comparatively to what is expected to be found nowadays. In fact, at present times, tritium figures have fallen lower than 5 TU in precipitation measured in the northern part of the country. Tritium content of precipitation was measured as 16 TU in 1992 on a single sample that was collected from the National Agency for Water Resources station in Ouargla. A major part of this rainfall evaporates back into the atmosphere that is unsaturated in moisture. Consequently, enrichment in tritium happens as water evaporates back. The lightest fractions (isotopes) are the ones that escape first causing enriching the remaining fraction in tritium. The 16 TU value would thus correspond to a rainy event that had happened during the field campaign (5, 6 Nov. 1992). It is the most representative value for that region and for that time. Unfortunately, all the other stations (Algiers, Ankara, and Tenerife) (Martinelli et al., 2014) are subject to a completely different climatic regime and besides the fact that they have more recent values, can absolutely not be used for our case. Therefore all the assumptions based on recent tritium rain values do not apply to this study.
Depleted contents in $^{18}$O and low tritium concentrations for phreatic waters fit well the mixing scheme and confirm the contribution from the older and deeper CI/CT groundwaters. The affected areas were clearly identified in the field and correspond to locations that are subject to a recycling and a return of irrigation waters whose origin are CI/CT boreholes. Moreover, the mixing that is clearly brought to light by the Cl$^-$ vs. $^{18}$O diagrams (Fig. 13 and 14) could partly derive from an ascending drainage from the deep and confined CI aquifer (exhibiting depleted homogenous $^{18}$O contents and very low tritium), a vertical leakage that is favoured by the Amguid El-biod highly faulted area (Guendouz and Moulla, 1996; Edmunds et al., 2003; Guendouz et al., 2003; Moulla et al., 2012).

3.6. Inverse modeling

We assume that the relationship between $^{18}$O and Cl$^-$ data obtained in 1992 is stable with time, which is a logical assumption as times of transfer from CI to both CT and Phr are very long. Considering both $^{18}$O and Cl$^-$ data, CI, CT and Phr data populations can be categorized. The CI and CT do not show appreciable $^{18}$O variations, and can be considered as a single population. The Phr samples consist however of different populations: cluster I, with $\delta^{18}$O values close to -8, and small Cl$^-$ concentrations, more specifically less than 35 mmol L$^{-1}$; cluster II, with $\delta^{18}$O values larger than 3, and very large Cl$^-$ concentrations, more specifically larger than 4,000 mmol L$^{-1}$ (Table 6); intermediate Phr samples result from mixing between clusters I and II (mixing line in Fig. 13, mixing curve in Fig. 14) and from evaporation of cluster I (evaporation line in Fig. 14). The mass-balance modeling has shown that relatively few phases are required to derive observed changes in water chemistry and to account for the hydrochemical evolution in Ouargla’s region. The mineral phases’ selection is based upon geological descriptions and analysis of rocks and sediments from the area (OSS, 2003; Hamdi-Aïssa et al., 2004).

The inverse model was constrained so that mineral phases from evaporites including gypsum, halite, mirabilite, glauberite, sylvite and bloedite were set to dissolve until they reach saturation, and calcite, dolomite were set to precipitate once they reached saturation. Cation exchange reactions of Ca$^{2+}$, Mg$^{2+}$, K$^+$ and Na$^+$ on exchange sites were included in the model to check which cations are adsorbed or desorbed during the process. Dissolution and desorption contribute as positive terms in the mass balance, as elements are released in solution. On the other hand, precipitation and adsorption contribute as negative terms, while elements removed from the solution. CO$_2$(g) dissolution is considered by Phreeqc as a dissolution of a mineral, whereas CO$_2$(g) degassing is dealt with as if it were a mineral precipitation.

Inverse modelling leads to a quantitative assessment of the different solutes’ acquisition processes and a mass balance for the salts that are dissolved or precipitated from CI, CT and Phr groundwaters (Fig. 14, Table 7), as follows:

- Transition from CI to CT involves gypsum, halite and sylvite dissolution, and some ion exchange namely calcium and potassium fixation on exchange sites against magnesium release, with a very small and quite negligible amount of CO$_2$(g) degassing. The maximum elemental concentration fractional error equals 1%. The model consists of a minimum number of phases (i.e. 6 solid phases and CO$_2$(g)); Another model implies as well dolomite precipitation with the same fractional error;

- Transition from CT to an average water component of cluster I involves dissolution of halite, sylvite, and bloedite from Turonian evaporites, with a very tiny calcite precipitation. The maximum fractional error in elemental concentration is 4%. Another model implies
CO$_2$ escape from the solution, with the same fractional error. Large amounts of Mg$^{2+}$ and SO$_4^{2-}$ are released within the solution (Sharif et al., 2008; Li et al., 2010; Carucci et al., 2012);

- the formation of Phr cluster II can be modeled as being a direct dissolution of salts from the sebkha by rainwater with positive $\delta^{18}O$; the most concentrated water (P036 from Sebkhet Safiune) is taken here for cluster II, and pure water as rainwater. In a descending order of amount, halite, sylvite, gypsum and huntite are the minerals that are the most involved in the dissolution process. A small amount of calcite precipitates while some Mg$^{2+}$ are released versus K$^+$ fixation on exchange sites. The maximum elemental fractional error in the concentration is equal to 0.004%. Another model implies dolomite precipitation with some more huntite dissolving, instead of calcite precipitation, but salt dissolution and ion exchange are the same. Huntite, dolomite and calcite stoichiometries are linearly related, so both models can fit field data, but calcite precipitation is preferred compared to dolomite precipitation at low temperature;

- the origin of all phreatic waters can be explained by a mixing in variable proportions of cluster I and cluster II. For instance, waters from cluster I and cluster II can easily be separated by their $\delta^{18}O$ respectively close to $-8\%$ and $3.5\%$ (Fig. 13 and 14). Mixing the two clusters is of course not an inert reaction, but rather results in the dissolution and the precipitation of minerals. Inverse modeling is then used to compute both mixing rates and the extent of matter exchange between soil and solution. For example, a phreatic water (piezometer P068) with intermediate values ($\delta^{18}O = -3$ and [Cl$^-$] $\approx 2$ M) is explained by the mixing of 58% water from cluster I and 42% from cluster II. In addition, calcite precipitates, Mg$^{2+}$ fixes on exchange sites, against Na$^+$ and K$^+$, gypsum dissolves as well as a minor amount of huntite (Table 7). The maximum elemental concentration fractional error is 2.5% and the mixing fractions’ weighted $\delta^{18}O$ is $-3.17\%$, which is very close to the measured value ($-3.04\%$). All the other models, making use of a minimum number of phases, and not taking into consideration ion exchange reactions are not found compatible with isotope data. Mixing rates obtained with such models are for example 98% of cluster I and 0.9% of cluster II, which leads to a $\delta^{18}O = (-7.80\%)$ which is quite far for the real measured value ($-3.04\%$).

The main types of groundwaters occurring in Ouargla basin are thus explained and could quantitatively be reconstructed. An exception is however sample P115, which is located exactly on the evaporation line of Phr cluster I. Despite numerous attempts, it could not be quantitatively rebuilt. Its $^3$H value (6.8) indicates that it is derived from a more or less recent water component with very small salt content, most possibly affected by rainwater and some preferential flow within the piezometer. As this is the only sample on this evaporation line, there remains a doubt on its significance.

Globally, the summary of mass transfer reactions occurring in the studied system (Table 7) shows that gypsum dissolution results in calcite precipitation and CO$_2$ escape, thus acting as an inorganic carbon sink.

4. CONCLUSIONS

From the three aquifers studied here, two (Complexe Terminal) and (Continental Intercalaire) are the main aquifers of Sahara, by the extent (thousands of km from the recharge area to the Gulf
of Gabès) and time of transfer (thousands of years). The last one, Phreatic aquifer, is shallow. The chemical facies have long been qualitatively described. Our results explain for the first time quantitatively the processes that occur during upward leakage through interaction between solution and the mineral constituents of the aquifers, and ultimately by mixing with surface waters. The hydrochemical study of the aquifer system occurring in Ouargla’s basin allowed us to identify the origin of its mineralization. Waters exhibit two different facies: sodium chloride and sodium sulfate for the phreatic aquifer (Phr), sodium sulfate for the Complexe Terminal (CT) aquifer and sodium chloride for the Continental Intercalaire (CI) aquifer. Calcium carbonate precipitation and evaporite dissolution explain the facies change from carbonate to sodium chloride or sodium sulfate that is recorded. However, reactions imply many minerals with common ions, deep reactions without evaporation as well as shallow processes affected by both evaporation and mixing. Those processes are separated by considering both chemical and isotopic data, and quantitatively explained making use of an inverse geochemical modeling. The latter was applied for the first time ever in Algeria, to an extreme environment, featured by a lack of data on a scarce natural resource such as Saharan groundwater. This methodology brought added-value to the comprehension of the processes occurring within the studied groundwaters on which the populations of the region rely for their daily consumption as well as for their agriculture directed mainly towards the culture of the main product of such an area that is dates besides at a lower extent other sub-products such as vegetables within the date-palms groves themselves. Results obtained through inverse modeling could help water resources’ managers both at the local and the regional scales, to gather the necessary information for an integrated management of that vital resource. Moreover and regarding the large geographic scale of the aquifers, such a pilot study could be taken as a support work to further investigations elsewhere in similar regions. The present study leads to the main result that phreatic waters do not originate simply from infiltration of rainwater and dissolution of salts from the sebkhas. Conversely, Phr waters are largely influenced by the upwardly mobile deep CT and CI groundwaters, fractions of the latter interacting with evaporites from the Turonian formations. Phreatic waters occurrence is explained as a mixture of two end-member components: cluster I, which is very close to CI and CT, and cluster II, which is highly mineralized and results from the dissolution by rainwater of salts from the sebkhas. At depth, CI leaks upwardly and dissolves gypsum, halite and sylvite, with some ion exchange, to give waters of CT aquifer composition. CT transformation into Phr cluster I waters involves the dissolution of Turonian evaporites (halite, sylvite and bloedite) with minor calcite precipitation. At the surface, direct dissolution by rainwater of salts from sebkhas (halite, sylvite, gypsum and some huntite) with precipitation of calcite and Mg\(^{2+}/K^+\) ion exchange results in cluster II Phr composition.

All phreatic groundwaters result from a mixing of cluster I and cluster II water that is accompanied by calcite precipitation, fixation of Mg\(^{2+}\) on ion exchange sites against the release of K\(^+\) and Na\(^+\). Moreover, some CO\(_2\) escapes from the solution at depth, but dissolves much more at the surface. The most complex phenomena occur during the dissolution of Turonian evaporites while CI leaks upwardly towards CT, and from Phr I to Phr II, while the transition from CT to Phr I implies a very limited number of phases. Globally, gypsum dissolution and calcite precipitation processes both act as an inorganic carbon sink.
ACKNOWLEDGEMENTS

The authors wish to thank the staff members of the National Agency for Water Resources in Ouargla (ANRH) and the Laboratory of Algerian Waters (ADE) for the support provided to the Technical Cooperation programme within which this work was carried out. Analyses of $^{18}$O were funded by the project CDTN / DDHI (Guendouz and Moulla, 1996). The supports of University of Ouargla and of INRA for travel grants of R. Slimani and G. Bourrié are gratefully acknowledged too.

APPENDIX

According to a simple Rayleigh equation, the evolution of the heavy isotope ratio in the remaining liquid $R_l$ is given by:

$$R_l \approx R_{l0} \times f_l^{\alpha-1},$$

where $f_l$ is the fraction remaining liquid and $\alpha$ the fractionation factor.

The fraction remaining liquid is derived from chloride concentration, as chloride can be considered as conservative during evaporation: all phreatic waters are undersaturated with respect to halite, that precipitates only in the last stage. Hence, the following equation holds:

$$f_l \equiv \frac{n_{w,1}}{n_{w,0}} = \frac{[Cl^-]_0}{[Cl^-]_t}.$$  

By taking natural logarithms, one obtains:

$$\ln R_l \approx (1 - \alpha) \times \ln [Cl^-] + \text{constant},$$

As, by definition,

$$R_l \equiv R_{std} \times (1 + \frac{\delta^{18}O}{1000}),$$

one has:

$$\ln R_l \equiv \ln R_{std} + \ln(1 + \frac{\delta^{18}O}{1000}),$$

$$\approx \ln R_{std} + \frac{\delta^{18}O}{1000},$$

hence, with base 10 logarithms:

$$\delta^{18}O \approx 1000(1 - \alpha) \log[Cl^-] + \text{constant},$$

$$\approx -\epsilon \log[Cl^-] + k,$$

where as classically defined $\epsilon = 1000(\alpha - 1)$ is the enrichment factor.
References


Foster, S., Margat, J., Droubi, A., 2006. Concept and importance of nonrenewable resources. Number 10 in IHP-VI Series on Groundwater, UNESCO.


13

| Location | Site | Aquifer | Lat. Long. Elev. | Date | EC | T | pH | Alk. | CT | SO\textsubscript{4} | Na\textsuperscript{+} | K\textsuperscript{+} | Mg\textsuperscript{2+} | Ca\textsuperscript{2+} | Br\textsuperscript{−} |
|----------|-----|---------|-----------------|------|----|---|---|------|-----|------|------|------|-------|------|------|-------|
| Hadd el I | D1F8 | M | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 3.5 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Hadd el I | D1F9 | M | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Hadd el I | D1F10 | S | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 3.5 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Rouissat | D3F8 | M | 3,534,310 724,290 140 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Amarat Moussa | D2F9 | M | 3,488,986 721,076 132 | 22/02/2013 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Hadd el I | D1F8 | M | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 3.5 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Hadd el I | D1F9 | M | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Amarat Moussa | D2F9 | M | 3,488,986 721,076 132 | 22/02/2013 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Chaf Charif | D4F10 | S | 3,534,670 722,140 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Fes | D6F10 | S | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Fes | D6F11 | S | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Hadd el I | D1F8 | M | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 3.5 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Hadd el I | D1F9 | M | 3,534,770 723,086 134 | 09/11/2012 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |
| Amarat Moussa | D2F9 | M | 3,488,986 721,076 132 | 22/02/2013 | 2.0 | 48.5 | 7.6 | 4.8 | 5.8 | 6.8 | 10.7 | 0.4 | 2.5 | 3.3 | 0.044 |

Table 1: Field and analytical data for the Continental Intercalaire aquifer.
Table 3: Field and analytical data for the Phreatic aquifer.

<table>
<thead>
<tr>
<th>Location</th>
<th>Site (&lt;x&gt;4-digit number)</th>
<th>Lat. (°)</th>
<th>Long. (°)</th>
<th>Elv (m)</th>
<th>Date (DD/MM/YYYY)</th>
<th>EC (mS/cm)</th>
<th>T (°C)</th>
<th>pH</th>
<th>Alk (mg/L)</th>
<th>Ca^2+ (mg/L)</th>
<th>Mg^2+ (mg/L)</th>
<th>K^+ (mg/L)</th>
<th>Na^+ (mg/L)</th>
<th>Cl^− (mg/L)</th>
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<td>9.2</td>
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<td>Am Khan</td>
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<td>17.0074</td>
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<td>28/03/2015</td>
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<td>24.2</td>
<td>8.1</td>
<td>2.0</td>
<td>13.7</td>
<td>8.1</td>
<td>1.8</td>
<td>4.5</td>
<td>3.2</td>
</tr>
<tr>
<td>Mekhadma</td>
<td>PL53</td>
<td>21.8436</td>
<td>67.8845</td>
<td>1992</td>
<td>28/03/2015</td>
<td>2.0</td>
<td>24.0</td>
<td>8.1</td>
<td>3.0</td>
<td>14.2</td>
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<td>67.8845</td>
<td>1992</td>
<td>28/03/2015</td>
<td>2.0</td>
<td>24.0</td>
<td>8.1</td>
<td>3.0</td>
<td>14.4</td>
<td>7.9</td>
<td>2.0</td>
<td>4.5</td>
<td>3.4</td>
</tr>
</tbody>
</table>

Note: EC (electric conductivity), T (temperature), pH, Alk (alkalinity), Ca^2+ (calcium), Mg^2+ (magnesium), K^+ (potassium), Na^+ (sodium), Cl^− (chloride).
For longitude and latitude, the reference is UTM 31 projection for North Sahara 1959 (CLARKE 1880 ellipsoid).

Table 4: Field and analytical data for the Phreatic aquifer (continued).

| Location          | Site | Lat. | Long. | Elev. | Date | EC  * | T     | pH  | Alk | Ca | Mg | Na | K | Br | SiO2 5 | SO4 2- | NO3 1- | Cl 1+ | Fe | CO2 3- | Ca2+ | Mg2+ | Ba | Sr |
|-------------------|------|------|-------|-------|------|------|------|-----|-----|----|----|----|---|---|-----|------|-------|-------|-----|---|--------|-----|-----|---|---|
|                  |      |      |       |       |      |      |      |     |     |    |    |    |   |   |     |      |       |       |     |   |        |     |     |   |   |
|                  |      |      |       |       |      |      |      |     |     |    |    |    |   |   |     |      |       |       |     |   |        |     |     |   |   |
|                  |      |      |       |       |      |      |      |     |     |    |    |    |   |   |     |      |       |       |     |   |        |     |     |   |   |
|                  |      |      |       |       |      |      |      |     |     |    |    |    |   |   |     |      |       |       |     |   |        |     |     |   |   |

For longitude and latitude, the reference is UTM 31 projection for North Sahara 1959 (CLARKE 1880 ellipsoid).
Table 5: Isotopic data $^{18}$O and $^3$H and chloride concentration in Continental Intercalaire, Complexe Terminal and Phreatic aquifers (sampling campaign in 1992).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^{18}$O</th>
<th>$^3$H</th>
<th>Parameter</th>
<th>$^{18}$O</th>
<th>$^3$H</th>
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<td>UT</td>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
</tr>
<tr>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
</tr>
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</table>

Phreatic aquifer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^{18}$O</th>
<th>$^3$H</th>
<th>Parameter</th>
<th>$^{18}$O</th>
<th>$^3$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
</tr>
<tr>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
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</table>

Complexe Terminal aquifer

<table>
<thead>
<tr>
<th>Parameter</th>
<th>$^{18}$O</th>
<th>$^3$H</th>
<th>Parameter</th>
<th>$^{18}$O</th>
<th>$^3$H</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
</tr>
<tr>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
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Continental Intercalaire aquifer

<table>
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<th>Parameter</th>
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<th>$^3$H</th>
<th>Parameter</th>
<th>$^{18}$O</th>
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<td>$\delta$</td>
<td>mol/L</td>
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<td>UT</td>
<td>$\delta$</td>
<td>mol/L</td>
<td>UT</td>
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</tbody>
</table>

Table 6: Statistical parameters for Continental Intercalaire (CI), Complexe Terminal (CT) and Phreatic (Phr) aquifers samples selected on the basis of $^{18}$O and CT $\delta$ data (see text).

<table>
<thead>
<tr>
<th>Aquifer</th>
<th>Size</th>
<th>Parameter</th>
<th>DC</th>
<th>T $^\circ$C</th>
<th>pH</th>
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<td>4.7</td>
<td>10.3</td>
<td>0.5</td>
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<td>2.4</td>
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<tr>
<td>CT</td>
<td>50</td>
<td>Skdd dev</td>
<td>3.9</td>
<td>21.0</td>
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<td>5.5</td>
<td>5.6</td>
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<tr>
<td>Phr ch1</td>
<td>26</td>
<td>Average</td>
<td>2.0</td>
<td>24.0</td>
<td>7.9</td>
<td>2.3</td>
<td>24.7</td>
<td>11.8</td>
<td>26.2</td>
<td>2.5</td>
<td>9.7</td>
<td>5.2</td>
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<tr>
<td>Phr ch2</td>
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<td>24.7</td>
<td>11.8</td>
<td>26.2</td>
<td>2.5</td>
<td>9.7</td>
<td>5.2</td>
</tr>
</tbody>
</table>
Table 7: Summary of mass transfer for geochemical inverse modeling. Phases and thermodynamic database are from Phreeqc 3.0 (Parkhurst and Appelo, 2013).

<table>
<thead>
<tr>
<th>Phases</th>
<th>Stoichiometry</th>
<th>CLCT</th>
<th>CT/Phr I</th>
<th>Rainwater/PhrI036</th>
<th>PhrI/PhrII60%/40%</th>
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</thead>
<tbody>
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<td>Calcite</td>
<td>CaCO$_3$</td>
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<td>–6.62 x 10^{-6}</td>
<td>–1.88 x 10^{-1}</td>
<td>–2.26 x 10^{-1}</td>
</tr>
<tr>
<td>CO$_2$(g)</td>
<td>CO$_2$</td>
<td>–5.88 x 10^{-3}</td>
<td>–</td>
<td>8.42 x 10^{-4}</td>
<td>5.77 x 10^{-4}</td>
</tr>
<tr>
<td>Gypsum</td>
<td>CaSO$_4$·2H$_2$O</td>
<td>4.33 x 10^{-3}</td>
<td>–</td>
<td>1.55 x 10^{-4}</td>
<td>1.67 x 10^{-4}</td>
</tr>
<tr>
<td>Halite</td>
<td>NaCl</td>
<td>7.05 x 10^{-3}</td>
<td>3.76 x 10^{-3}</td>
<td>6.72</td>
<td>1.28</td>
</tr>
<tr>
<td>Sylvite</td>
<td>KCl</td>
<td>2.18 x 10^{-3}</td>
<td>1.08 x 10^{-3}</td>
<td>4.02 x 10^{-4}</td>
<td>–</td>
</tr>
<tr>
<td>Bloedite</td>
<td>Na$_2$Mg(SO$_4$)$_2$·4$H_2$O</td>
<td>–</td>
<td>1.44 x 10^{-3}</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Hunsite</td>
<td>CaMg$_2$(CO$_3$)$_4$·$H_2$O</td>
<td>–</td>
<td>–</td>
<td>4.74 x 10^{-2}</td>
<td>5.65 x 10^{-2}</td>
</tr>
<tr>
<td>Ca ion exchange</td>
<td>CaX</td>
<td>–1.11 x 10^{-3}</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Mg ion exchange</td>
<td>MgX$_2$</td>
<td>1.96 x 10^{-3}</td>
<td>–</td>
<td>1.75 x 10^{-4}</td>
<td>2.02 x 10^{-4}</td>
</tr>
<tr>
<td>Na ion exchange</td>
<td>NaX</td>
<td>–</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>K ion exchange</td>
<td>KX</td>
<td>–1.69 x 10^{-3}</td>
<td>–</td>
<td>–3.49 x 10^{-4}</td>
<td>1.20 x 10^{-2}</td>
</tr>
</tbody>
</table>

Values are in mol/kg (H$_2$O). Positive (mass entering solution) and negative (mass leaving solution) phase mole transfers indicate dissolution and precipitation, respectively; — indicates no mass transfer.
Figure 1: Location and schematic relations of aquifers in Ouargla.
Blue lines represent limits between aquifers, and the names of aquifers are given in bold letters; as the limit between Senonian and Mio-pliocene aquifers is not well defined, a dashed blue line is used. Names of villages and cities are given in roman (Bamendil, Ouargla, Sidi Khouiled), while geological/geomorphological features are in italic (Glacis, Sebkha, Chott, Dunes). Depths are relative to the ground surface. Letters a and b refer to the cross section (fig. 2) and to the localisation map (fig. 3).

Figure 2: Geologic cross section in the region of Ouargla.
The blue pattern used for Chott and Sebkha correspond to the limit of the saturated zone.
Figure 3: Location map of sampling points
Figure 4: Piper diagram for Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles).
Figure 5: Contour maps of the salinity (expressed as global mineralization) in the aquifer system, (a) Phreatic aquifer; (b) and (c) Complexe Terminal [(b) Mio-pliocene and (c) Senonian]; figures are isovalues of global mineralization (values in g/L).
Figure 6: Equilibrium diagrams of calcite (top) and gypsum (bottom) for Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles). Equilibrium lines are defined as: $\log\left[\text{Ca}^{2+}\right] + \log\left[\text{CO}_3^{2-}\right] = \log K_{sp}$ for calcite, and $\log\left[\text{Ca}^{2+}\right] + 2 \log\left[\text{H}_2\text{O}\right] + \log\left[\text{SO}_4^{2-}\right] = \log K_{sp}$ for gypsum.
Figure 7: Variation of saturation indices with distance from south to north in the region of Ouargla.
Figure 8: Change from carbonate facies to evaporite from Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles).

Figure 9: Change from sulfate facies to chloride from Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles).
Figure 10: Correlation between Na⁺ and Cl⁻ concentrations in Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles). Seawater composition (star) is [Na⁺] = 459.3 mmol L⁻¹ and [Cl⁻] = 535.3 mmol L⁻¹ (Stumm and Morgan, 1999, p.899).

Figure 11: Calcium vs. HCO₃⁻ diagram in Continental Intercalaire (filled squares), Complexe Terminal (open circles), Phreatic aquifer (open triangles) and Seawater composition (star) is [Ca²⁺] = 10.2 mmol L⁻¹ and [HCO₃⁻] = 2.38 mmol L⁻¹ (Stumm and Morgan, 1999, p.899).
Figure 12: Calcium vs. $\text{SO}_4^{2-}$ diagram in Continental Intercalaire (filled squares), Complexe Terminal (open circles), Phreatic aquifer (open triangles) and Seawater composition (star) is $[\text{Ca}^{2+}] = 10.2 \text{ mmol L}^{-1}$ and $[\text{SO}_4^{2-}] = 28.2 \text{ mmol L}^{-1}$ (Stumm and Morgan, 1999, p.899).

Figure 13: Chloride concentration versus $\delta^{18}O$ in Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles) from Ouargla.
Figure 14: Log [Cl⁻] concentration versus δ¹⁸O in Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles) from Ouargla.