

Geochemical inverse modeling of chemical and isotopic data from groundwaters in Sahara (Ouargla basin, Algeria)

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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Unpublished chemical and isotopic data taken in November 1992 from the three major Saharan aquifers namely, the “Continental Intercalaire” (CI), the “Complexe Terminal”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 a 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 only access to little or no renewable water resources. In many arid regions such as Sahara, groundwater is the only source of water supply for domestic, agricultural or industrial purposes, often causing overuse and / or degradation of water quality.

The groundwater resources of Ouargla basin (Lower-Sahara, Algerian) (Fig. 1) are contained in three main reservoirs (UNESCO, 1972; Eckstein and Eckstein, 2003; OSS, 2003, 2008):

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- 19 • at the top, the phreatic aquifer (Phr), located in sandy gypsum permeable formations of
20 Quaternary, is almost unexploited, due to its salinity (50 g/L);
- 21 • in the middle, the “Complexe Terminal” (CT) (Cornet and Gouscov, 1952; UNESCO,
22 1972) is the most exploited and includes several aquifers in different geological forma-
23 tions. Groundwater circulates in one or two lithostratigraphic formations of the Eocene
24 and Senonian carbonates or Mio-pliocene sands;
- 25 • at the bottom, the “Continental Intercalaire” (CI), hosted in the lower Cretaceous continen-
26 tal formations (Barremian and Albian), mainly composed of sandstones, sands and clays.
27 It is only partially exploited because of its significant depth.

28 After use, waters are discharged in a closed system (endorheic basin) and constitute a po-
29 tential hazard to the environment, to public health and may jeopardize the sustainability of agri-
30 culture, due to rising of the phreatic aquifer watertable, extension of soil salinization and so
31 on (Hamdi-Aïssa et al., 2004; Slimani, 2006). Several studies (Guendouz, 1985; Fontes et al.,
32 1986; Guendouz and Moulla, 1996; Edmunds et al., 2003; Guendouz et al., 2003; Hamdi-Aïssa
33 et al., 2004; Foster et al., 2006; OSS, 2008; Al-Gamal, 2011) started from chemical and isotopic
34 information (^2H , ^{18}O , ^{234}U , ^{238}U , ^{36}Cl) to characterize the relationships between aquifers. In
35 particular, such studies focused on the recharge of the deep CI aquifer system. These investi-
36 gations dealt particularly with water chemical facies, mapped isocontents of various parameters,
37 and reported typical geochemical ratios ($[\text{SO}_4^{2-}]/[\text{Cl}^-]$, $[\text{Mg}^{2+}]/[\text{Ca}^{2+}]$) as well as other correla-
38 tions. Minerals / solutions equilibria were checked by computing saturation indices with respect
39 to calcite, gypsum, anhydrite and halite, but processes were only qualitatively assessed.

40 The present study aims at applying for the first time ever in Algeria, ~~a new methodology~~
41 ~~(inverse modeling)~~ to an extreme environment ~~where~~ lack of data on a scarce natural resource
42 ~~(groundwater) is observed~~. New data were hence collected in order to characterize the hydro-
43 chemical and the isotopic composition of the major aquifers in the Saharan region of Ouargla.
44 New possibilities offered by progress in geochemical modeling were used. The objective was
45 also to identify the origin of the mineralization and the water-rock interactions that occur along
46 the flow. More specifically, inverse modeling of chemical reactions allows one to select the best
47 conceptual model for the interpretation of the geochemical evolution of Ouargla aquifer system.
48 The stepwise inversion strategy involves designing a list of scenarios (hypotheses) that take into
49 consideration the most plausible combinations of geochemical processes that may occur within
50 the studied medium. After resolving the scenarios in a stepwise manner, the one that provides
51 the best conceptual geochemical model is then selected (Dai et al., 2006). Inverse modeling
52 with Phreeqc 3.0 was used to quantitatively assess the influence of the processes that explain
53 the acquisition of solutes for the different aquifers: dissolution, precipitation, mixing and ion
54 exchange. This results in constraints on mass balances as well as on the exchange of matter
55 between aquifers.

56 2. METHODOLOGY

57 2.1. Presentation of the study area

58 The study area is located in the northeastern desert of Algeria “Lower-Sahara” (Le Houérou,
59 2009) near the city of Ouargla (Fig. 1), $31^\circ 54'$ to $32^\circ 1'$ N and $5^\circ 15'$ to $5^\circ 27'$ E, with a mean ele-
60 vation of 134 (m.a.s.l.). It is located in the quaternary valley of Oued Mya basin. Present climate

61 belongs to the arid Mediterranean-type (Dubief, 1963; Le Houérou, 2009; ONM, 1975/2013), as
62 it is characterized by a mean annual temperature of 22.5 °C, a yearly rainfall of 43.6 mm/yr and
63 a very high evaporation rate of 2,138 mm/yr.

64
65 Ouargla's region and the entire Lower Sahara has experienced during its long geological
66 history alternating marine and continental sedimentation phases. During Secondary era, vertical
67 movements affected the Precambrian basement causing in particular collapse of its central part,
68 along an axis passing approximately through the Oued Righ valley and the upper portion of the
69 valley oued Mya. According to Furon (1960), a epicontinental sea spread to the Lower Eocene of
70 northern Sahara. After the Oligocene, the sea gradually withdrew. It is estimated at present that
71 this sea did not reach Ouargla and transgression stopped at the edge of the bowl (Furon, 1960;
72 Lelièvre, 1969). The basin is carved into Mio-pliocene (MP) deposits, which alternate with red
73 sands, clays and sometimes marls; gypsum is not abundant and dated from Pontian (MP) (Cornet
74 and Gouscov, 1952; Dubief, 1953; Ould Baba Sy and Besbes, 2006). The continental Pliocene
75 consists of a local limestone crust with puddingstone or lacustrine limestone (Fig. 2), shaped
76 by eolian erosion into flat areas (regs). The Quaternary formations are lithologically composed
77 of alternating layers of permeable sand and relatively impermeable marl (Aumassip et al., 1972;
78 Chellat et al., 2014).

79 The exploitation of Mio-pliocene aquifer is ancient and at the origin of the creation of the
80 oasis (Lelièvre, 1969; Moulias, 1927). The piezometric level was higher (145 m a.s.l.) but over-
81 exploitation at the end of the XIXth century led to a catastrophic decrease of the resource, with
82 presently more than 900 boreholes (ANRH, 2011).

83 The exploitation of Senonian aquifer dates back to 1953 at a depth 140 m to 200 m depth,
84 with a small initial rate *ca.* 9 L s⁻¹; two boreholes have been exploited since 1965 and 1969, with
85 a total flowrate *ca.* 42 L s⁻¹, for drinking water and irrigation.

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

- 87 • El Hedeb I, 1,335 m deep, with a flowrate 141 L s⁻¹;
- 88 • El Hedeb II, 1,400 m deep, with a flowrate 68 L s⁻¹.

89 2.2. *Sampling and analytical methods*

90 The sampling programme consisted of collecting samples along transects corresponding to
91 directions of flow for both Phr and CT aquifers while it was possible to collect only eight samples
92 from the CI. A total of ~~(n = 107)~~ samples were collected during a field campaign in 2013, along
93 the main flowpath of Oued Mya. 67 of them were from piezometers tapping the phreatic aquifer,
94 32 from CT wells and the last 8 from boreholes tapping the CI aquifer (Fig. 3). Analyses of
95 Na⁺, K⁺, Ca²⁺, Mg²⁺, Cl⁻, SO₄²⁻ and HCO₃⁻ were performed by ion chromatography at Algiers
96 Nuclear Research Center (CRNA). Previous and yet unpublished data (Guendouz and Moulla,
97 1996) sampled in 1992 are used here too: 59 samples for Phr aquifer, 15 samples for CT aquifer
98 and 3 samples for the CI aquifer for chemical analyses, data ¹⁸O and ³H (Guendouz and Moulla,
99 1996).

100 2.3. *Geochemical method*

101 Phreeqc was used to check minerals / solution equilibria using the specific interaction the-
102 ory (SIT), *i.e.* the extension of Debye-Hückel law by Scatchard and Guggenheim incorporated
103 recently in Phreeqc 3.0 (Parkhurst and Appelo, 2013). Inverse modeling was used to calculate

104 the number of minerals and gases' moles that must respectively dissolve or precipitate/degas to
105 account for the difference in composition between initial and final water end members (Plum-
106 mer and Back, 1980; Kenoyer and Bowser, 1992; Deutsch, 1997; Plummer and Sprinckle, 2001;
107 Güler and Thyne, 2004; Parkhurst and Appelo, 2013). This mass balance technique has been
108 used to quantify reactions controlling water chemistry along flow paths (Thomas et al., 1989).
109 It is also used to quantify the mixing proportions of end-member components in a flow system
110 (Kuells et al., 2000; Belkhiri et al., 2010, 2012).

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

122 3. RESULTS AND DISCUSSION

123 Tables 1 to 5 illustrate the results of the chemical and the isotopic analyses. Samples are
124 ordered according to an increasing electric conductivity (EC), and this is assumed to provide
125 an ordering for increasing salt content. In both phreatic and CT aquifers, temperature is close to
126 25 °C, while for CI aquifer, temperature is close to 50 °C. The values presented in tables 1 to 5 are
127 raw analytical data that were corrected for defects of charge balance before computing activities
128 with Phreeqc. As analytical errors could not be ascribed to a specific analyte, the correction was
129 made proportionally. The corrections do not affect the anions to anions mole ratios such as for
130 $[\text{HCO}_3^-]/([\text{Cl}^-] + 2[\text{SO}_4^{2-}])$ or $[\text{SO}_4^{2-}]/[\text{Cl}^-]$, whereas they affect the cation to anion ratio such
131 as for $[\text{Na}^+]/[\text{Cl}^-]$.

132 3.1. *Characterization of chemical facies of the groundwater*

133 Piper diagrams drawn for the studied groundwaters (Fig. 4) broadly show a scatter plot dom-
134 inated by a Chloride-Sodium facies. However, when going into small details, the widespread
135 chemical facies of the Phr aquifer is closer to the NaCl cluster than those of CI and CT aquifers.
136 Respectively, CaSO_4 , Na_2SO_4 , MgSO_4 and NaCl are the most dominant chemical species (min-
137 erals) that are present in the phreatic waters. This sequential order of solutes is comparable to
138 that of other groundwater occurring in North Africa, and especially in the neighboring area of
139 the chotts (depressions where salts concentrate by evaporation) Merouane and Melrhir (Vallès
140 et al., 1997; Hamdi-Aïssa et al., 2004).

141 3.2. *Spatial distribution of the mineralization*

142 The salinity of the phreatic aquifer varies considerably depending on the location (namely,
143 the distance from wells or drains) and time (due to the influence of irrigation) (Fig. 5a).

144 Its salinity is low around irrigated and fairly well-drained areas, such as the palm groves of
145 Hassi Miloud, just north of Ouargla (Fig. 3) that benefit from freshwater and are drained to the

146 sebkha Oum el Raneb. However, the three lowest salinity values are observed in the wells of
147 Ouargla palm-grove itself, where the Phr aquifer watertable is deeper than 2 m.

148 Conversely, the highest salinity waters are found in wells drilled in the chotts and sebkhas (a
149 sebkha is the central part of a chott where salinity is the largest) (Safioune and Oum er Raneb)
150 where the aquifer is often shallower than 50 cm.

151 The salinity of the CT (Mio-pliocene) aquifer (Fig. 5b) is much lower than that of the Phr
152 aquifer, and ranges from 1 to 2 g/L; however, its hardness is larger and it contains more sulfate,
153 chloride and sodium than the waters of the Senonian formations and those of the CI aquifer. The
154 salinity of the Senonian aquifer ranges from 1.1 to 1.7 g/L, while the average salinity of the CI
155 aquifer is 0.7 g/L (Fig. 5c).

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

159 3.3. Saturation Indices

160 The calculated saturation indices (SI) reveal that waters from CI at 50 °C are close to equi-
161 librium with respect to calcite, except for 3 samples that are slightly oversaturated. They are
162 however all undersaturated with respect to gypsum (Fig. 6).

163 Moreover, they are oversaturated with respect to dolomite and undersaturated with respect to
164 anhydrite and halite (Fig. 7).

165 Waters from CT and phreatic aquifers show the same pattern, but some of them are more
166 largely oversaturated with respect to calcite, at 25 °C.

167 However, several phreatic waters (P031, P566, PLX4, PL18, P002, P023, P116, P066, P162
168 and P036) that are located in the sebkhas of Sefioune, Oum-er-Raneb, Bamendil and Ain el
169 Beida's chott are saturated with gypsum and anhydrite. This is in accordance with highly evapo-
170 rative environments found elsewhere (UNESCO, 1972; Hamdi-Aïssa et al., 2004; Slimani, 2006).

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

174 3.4. Change of facies from the carbonated cluster to the evaporites' cluster

175 The facies shifts progressively from the carbonated (CI and CT aquifers) to the evaporites'
176 one (Phr aquifer) with an increase in sulfates and chlorides at the expense of carbonates (SI of
177 gypsum, anhydrite and halite). This is illustrated by a decrease of $\frac{[\text{HCO}_3^-]}{([\text{Cl}^-] + 2[\text{SO}_4^{2-}])}$
178 (Fig. 8) from 0.2 to 0 and of $\frac{[\text{SO}_4^{2-}]}{[\text{Cl}^-]}$ from 0.8 to values ranging from 0.3 and 0 (Fig. 9)
179 while salinity increases. Carbonate concentrations tend towards very small values, while it is not
180 the case for sulfates. This is due to both gypsum dissolution and calcite precipitation.

181 Chlorides in groundwater may come from three different sources: (i) ancient sea water en-
182 trapped in sediments; (ii) dissolution of halite and related minerals that are present in evaporite
183 deposits and (iii) dissolution of dry fallout from the atmosphere, particularly in these arid regions
184 (Matiatos et al., 2014; Hadj-Ammar et al., 2014).

185 $[\text{Na}^+]/[\text{Cl}^-]$ ratio is from 0.85 to 1.26 for CI aquifer, from 0.40 to 1.02 for the CT aquifer
186 and from 0.13 to 2.15 for the Phr aquifer. All the measured points from the three considered
187 aquifers are more or less linearly scattered around the unity slope straight line that stands for
188 halite dissolution (Fig. 10). The latter appears as the most dominant reaction occurring in the

189 medium. However, at very high salinity, Na^+ seems to swerve from the straight line, towards
190 smaller values.

191 A further scrutiny of Fig. 10 shows that CI waters are very close to the 1:1 line. CT waters
192 are enriched in both Na^+ and Cl^- but slightly lower than the 1:1 line while phreatic waters are
193 largely enriched and much more scattered. CT waters are closer to the seawater mole ratio
194 (0.858), but some lower values imply a contribution from another source of chloride than halite
195 or from entrapped seawater. Conversely, a $[\text{Na}^+]/[\text{Cl}^-]$ ratio larger than 1 is observed for phreatic
196 waters, which implies the contribution of another source of sodium, most likely sodium sulfate,
197 that is present as mirabilite or thenardite in the chotts and the sebkhas areas.

198 $[\text{Br}^-]/[\text{Cl}^-]$ ratio ranges from 2×10^{-3} to 3×10^{-3} . The value of this molar ratio for halite is
199 around 2.5×10^{-3} , which matches the aforementioned range and confirms that halite dissolution
200 is the most dominant reaction taking place in the studied medium.

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

207 In this case, a cation exchange process seems to occur and lead to a preferential adsorption
208 of divalent cations, with a release of Na^+ . This is confirmed by the inverse modeling that is
209 developed below and which implies Mg^{2+} fixation and Na^+ and K^+ releases.

210 Larger sulfate values observed in the phreatic aquifer (Fig. 12) with $[\text{Ca}^{2+}]/[\text{SO}_4^{2-}] < 1$ can
211 be attributed to a Na-Mg sulfate dissolution from a mineral bearing such elements. This is for
212 instance the case of bloedite.

213

214 3.5. Isotope geochemistry

215 CT and CI aquifer exhibit depleted and homogeneous ^{18}O contents, ranging from -8.32‰
216 to -7.85‰ . This was already previously reported by many authors (Edmunds et al., 2003;
217 Guendouz et al., 2003; Moulla et al., 2012). On the other hand, ^{18}O values for the phreatic
218 aquifer are widely dispersed and vary between -8.84‰ to 3.42‰ (Table 6). Waters located
219 north of the virtual line connecting approximately Hassi-Miloud to sebkhet Safioune, are found
220 more enriched in heavy isotopes and are thus more evaporated. In that area, water table is close to
221 the surface and mixing of both CI and CT groundwaters with phreatic ones through irrigation is
222 nonexistent. Conversely, waters located south of Hassi Miloud up to Ouargla city show depleted
223 values. This is the clear fingerprint of a contribution to the Phr waters from the underlying CI
224 and CT aquifers (Gonfiantini et al., 1975; Guendouz, 1985; Fontes et al., 1986; Guendouz and
225 Moulla, 1996).

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

231 Cluster I represents the waters from CI and CT whose isotopic composition is depleted
232 in ^{18}O (average value around -8.2‰) (Fig. 13). They correspond to an old water recharge
233 (palæorecharge); whose age estimated by means of ^{14}C , exceeds 15.000 years BP (Guendouz,

234 1985; Guendouz and Michelot, 2006). So, it is not a water body that is recharged by recent
 235 precipitation. It consists of CI and CT groundwaters and partly of phreatic waters, and can be
 236 ascribed to an upward leakage favored by the extension of faults near Amguid El-Biod dorsal.

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

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

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

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

242 where α is the fractionation factor during evaporation, $\epsilon \equiv -1000 \times (1 - \alpha)$ is the enrichment
 243 factor and k is a constant (Ma et al., 2010; Chkir et al., 2009).

244 CI and CT waters are better separated in the semi-logarithmic plot because they are differen-
 245 tiated by their chloride content. According to equation (1), simple evaporation gives a straight
 246 line (solid line in Fig. 14). The value of ϵ used is the value at 25 °C, which is equal to -73.5 .

247 P115 is the only sample that appears on the straight evaporation line (Fig. 14). It should be
 248 considered as an outlier since the rest of the samples are all well aligned on the logarithmic fit
 249 derived from the mixing line of Figure 13.

250 The phreatic waters that are close to cluster I (Fig. 13) correspond to groundwaters oc-
 251 ccurring in the edges of the basin (Hassi Miloud, piezometer P433) (Fig. 14). They are low-
 252 mineralized and acquire their salinity via two processes, namely: dissolution of evaporites along
 253 their underground transit up to Sebkhet Safioune and dilution through upward leakage by the
 254 less-mineralized waters of CI and CT aquifers (for example Hedeb I for CI and D7F4 for CT)
 255 (Fig. 14) (Guendouz, 1985; Guendouz and Moulla, 1996).

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

259 The δ value of the mixture is given by:

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

260 where f is the fraction of CI aquifer, $1 - f$ the fraction of the CT and δ_1, δ_2 are the respective
 261 isotope contents.

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

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

270 Turonian evaporites are found to lie in between CI deep aquifer and the Senonian and Miocene
 271 formations bearing CT aquifer. CT waters can thus simply originate from ascending CI waters
 272 that dissolve Turonian evaporites, a process which does not involve any change in ^{18}O content.
 273 Conversely, phreatic waters result to a minor degree from evaporation and mostly from dissolu-
 274 tion of sebkhas evaporites by ^{18}O enriched rainwater and mixing with CI-CT waters.

275 *3.5.1. Tritium content of water*

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

280 These values are dated back to November 1992 so they are old values and they are considered
281 high comparatively to what is expected to be found nowadays. In fact, at present times, tritium
282 figures have fallen lower than 5 TU in precipitation measured in the northern part of the country.

283 Tritium content of precipitation was measured as 16 TU in 1992 on a single sample that was
284 collected from the National Agency for Water Resources station in Ouargla. A major part of
285 this rainfall evaporates back into the atmosphere that is unsaturated in moisture. Consequently,
286 enrichment in tritium happens as water evaporates back. The lightest fractions (isotopes) are
287 the ones that escape first causing enriching the remaining fraction in tritium. The 16 TU value
288 would thus correspond to a rainy event that had happened during the field campaign (5, 6 Nov.
289 1992). It is the most representative value for that region and for that time. Unfortunately, all the
290 other stations (Algiers, Ankara, and Tenerife) (Martinelli et al., 2014) are subject to a completely
291 different climatic regime and besides the fact that they have more recent values, can absolutely
292 not be used for our case. Therefore all the assumptions based on recent tritium rain values do not
293 apply to this study.

294 Depleted contents in ^{18}O and low tritium concentrations for phreatic waters fit well the mix-
295 ing scheme and confirm the contribution from the older and deeper CI/CT groundwaters. The
296 affected areas were clearly identified in the field and correspond to locations that are subject to
297 a recycling and a return of irrigation waters whose origin are CI/CT boreholes. Moreover, the
298 mixing that is clearly brought to light by the Cl^- vs. ^{18}O diagrams (Fig. 13 and 14) could partly
299 derive from an ascending drainage from the deep and confined CI aquifer (exhibiting depleted ho-
300 mogenous ^{18}O contents and very low tritium), a vertical leakage that is favoured by the Amguid
301 El-biod highly faulted area (Guendouz and Moulla, 1996; Edmunds et al., 2003; Guendouz et al.,
302 2003; Moulla et al., 2012).

303 *3.6. Inverse modeling*

304 We assume that the relationship between ^{18}O and Cl^- data obtained in 1992 is stable with
305 time, which is a logical assumption as times of transfer from CI to both CT and Phr are very long.
306 Considering both ^{18}O and Cl^- data, CI, CT and Phr data populations can be categorized. The CI
307 and CT do not show appreciable ^{18}O variations, and can be considered as a single population. The
308 Phr samples consist however of different populations: cluster I, with $\delta^{18}\text{O}$ values close to -8, and
309 small Cl^- concentrations, more specifically less than 35 mmol L^{-1} ; cluster II, with $\delta^{18}\text{O}$ values
310 larger than 3, and very large Cl^- concentrations, more specifically larger than $4,000 \text{ mmol L}^{-1}$
311 (Table 7); intermediate Phr samples result from mixing between clusters I and II (mixing line in
312 Fig. 13, mixing curve in Fig. 14) and from evaporation of cluster I (evaporation line in Fig. 14).

313 The mass-balance modeling has shown that relatively few phases are required to derive ob-
314 served changes in water chemistry and to account for the hydrochemical evolution in Ouargla's
315 region. The mineral phases' selection is based upon geological descriptions and analysis of rocks
316 and sediments from the area (OSS, 2003; Hamdi-Aïssa et al., 2004).

317 The inverse model was constrained so that mineral phases from evaporites including gypsum,
318 halite, mirabilite, glauberite, sylvite and bloedite were set to dissolve until they reach saturation,
319 and calcite, dolomite were set to precipitate once they reached saturation. Cation exchange reac-
320 tions of Ca^{2+} , Mg^{2+} , K^+ and Na^+ on exchange sites were included in the model to check which

321 cations are adsorbed or desorbed during the process. Dissolution and desorption contribute as
322 positive terms in the mass balance, as elements are released in solution. On the other hand,
323 precipitation and adsorption contribute as negative terms, while elements removed from the so-
324 lution. $\text{CO}_{2(g)}$ dissolution is considered by Phreeqc as a dissolution of a mineral, whereas $\text{CO}_{2(g)}$
325 degassing is dealt with as if it were a mineral precipitation.

326 Inverse modelling leads to a quantitative assessment of the different solutes' acquisition pro-
327 cesses and a mass balance for the salts that are dissolved or precipitated from CI, CT and Phr
328 groundwaters (Fig. 14, Table 8), as follows:

- 329 • transition from CI to CT involves gypsum, halite and sylvite dissolution, and some ion
330 exchange namely calcium and potassium fixation on exchange sites against magnesium
331 release, with a very small and quite negligible amount of $\text{CO}_{2(g)}$ degassing. The maximum
332 elemental concentration fractional error equals 1%. The model consists of a minimum
333 number of phases (*i.e.* 6 solid phases and $\text{CO}_{2(g)}$); Another model implies as well dolomite
334 precipitation with the same fractional error;
- 335 • transition from CT to an average water component of cluster I involves dissolution of
336 halite, sylvite, and bloedite from Turonian evaporites, with a very tiny calcite precipitation.
337 The maximum fractional error in elemental concentration is 4%. Another model implies
338 $\text{CO}_{2(g)}$ escape from the solution, with the same fractional error. Large amounts of Mg^{2+}
339 and SO_4^{2-} are released within the solution (Sharif et al., 2008; Li et al., 2010; Carucci
340 et al., 2012);
- 341 • the formation of Phr cluster II can be modeled as being a direct dissolution of salts from the
342 sebkha by rainwater with positive $\delta^{18}\text{O}$; the most concentrated water (P036 from Sebkhet
343 Safioune) is taken here for cluster II, and pure water as rainwater. In a descending order
344 of amount, halite, sylvite, gypsum and huntite are the minerals that are the most involved
345 in the dissolution process. A small amount of calcite precipitates while some Mg^{2+} are
346 released versus K^+ fixation on exchange sites. The maximum elemental fractional error in
347 the concentration is equal to 0.004%. Another model implies dolomite precipitation with
348 some more huntite dissolving, instead of calcite precipitation, but salt dissolution and ion
349 exchange are the same. Huntite, dolomite and calcite stoichiometries are linearly related,
350 so both models can fit field data, but calcite precipitation is preferred compared to dolomite
351 precipitation at low temperature;
- 352 • the origin of all phreatic waters can be explained by a mixing in variable proportions
353 of cluster I and cluster II. For instance, waters from cluster I and cluster II can easily be
354 separated by their $\delta^{18}\text{O}$ respectively close to -8‰ and 3.5‰ (Fig. 13 and 14). Mixing the
355 two clusters is of course not an inert reaction, but rather results in the dissolution and the
356 precipitation of minerals. Inverse modeling is then used to compute both mixing rates and
357 the extent of matter exchange between soil and solution. For example, a phreatic water
358 (piezometer P068) with intermediate values ($\delta^{18}\text{O} = -3$ and $[\text{Cl}^-] \simeq 2\text{ M}$) is explained
359 by the mixing of 58% water from cluster I and 42% from cluster II. In addition, calcite
360 precipitates, Mg^{2+} fixes on exchange sites, against Na^+ and K^+ , gypsum dissolves as well
361 as a minor amount of huntite (Table 8). The maximum elemental concentration fractional
362 error is 2.5% and the mixing fractions' weighted the $\delta^{18}\text{O}$ is -3.17‰ , which is very
363 close to the measured value (-3.04‰). All the other models, making use of a minimum
364 number of phases, and not taking into consideration ion exchange reactions are not found

365 compatible with isotope data. Mixing rates obtained with such models are for example
366 98% of cluster I and 0.9% of cluster II, which leads to a $\delta^{18}O = (-7.80 \text{‰})$ which is quite
367 far for the real measured value (-3.04‰).

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

375 Globally, the summary of mass transfer reactions occurring in the studied system (Table 8)
376 shows that gypsum dissolution results in calcite precipitation and $CO_{2(g)}$ dissolution, thus acting
377 as an inorganic carbon sink.

378 4. CONCLUSIONS

379 Groundwater hydrochemistry is a good record indicator for the water-rock interactions that
380 occur along the groundwater flowpath. The mineral load reflects well the complex processes
381 taking place while water circulates underground since its point of infiltration.

382 The hydrochemical study of the aquifer system occurring in Ouargla's basin allowed us to
383 identify the origin of its mineralization. Waters exhibit two different facies: sodium chloride and
384 sodium sulfate for the phreatic aquifer (Phr), sodium sulfate for the Complexe Terminal (CT)
385 aquifer and sodium chloride for the Continental Intercalaire (CI) aquifer. Calcium carbonate
386 precipitation and evaporite dissolution explain the facies change from carbonate to sodium chlo-
387 ride or sodium sulfate. However reactions imply many minerals with common ions, deep reac-
388 tions without evaporation as well as shallow processes affected by both evaporation and mixing.
389 Those processes are separated by considering both chemical and isotopic data, and quantitatively
390 explained making use of an inverse geochemical modeling. The main result is that Phr waters
391 do not originate simply from infiltration of rainwater and dissolution of salts from the sebkhas.
392 Conversely, Phr waters are largely influenced by the upwardly mobile deep CT and CI groundwa-
393 ters, fractions of the latter interacting with evaporites from Turonian formations. Phreatic waters
394 occurrence is explained as a mixing of two end-member components: cluster I, which is very
395 close to CI and CT, and cluster II, which is highly mineralized and results from the dissolution
396 by rainwater of salts from the sebkhas.

397 At depth, CI leaks upwardly and dissolves gypsum, halite and sylvite, with some ion ex-
398 change, to give waters of CT aquifer composition.

399 CT transformation into Phr cluster I waters involves the dissolution of Turonian evaporites
400 (halite, sylvite and bloedite) with minor calcite precipitation.

401 At the surface, direct dissolution by rainwater of salts from sebkhas (halite, sylvite, gypsum
402 and some huntite) with precipitation of calcite and Mg^{2+}/K^+ ion exchange results in cluster II
403 Phr composition.

404 All phreatic groundwaters result from a mixing of cluster I and cluster II water that is accom-
405 panied by calcite precipitation, fixation of Mg^{2+} on ion exchange sites against the release of K^+
406 and Na^+ .

407 Moreover, some $CO_{2(g)}$ escapes from the solution at depth, but dissolves much more at the
408 surface. The most complex phenomena occur during the dissolution of Turonian evaporites while

409 CI leaks upwardly towards CT, and from Phr I to Phr II, while the transition from CT to Phr I
 410 implies a very limited number of phases. Globally, gypsum dissolution and calcite precipitation
 411 processes both act as an inorganic carbon sink.

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419 APPENDIX

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

$$R_l \approx R_{l,0} \times f_l^{\alpha-1}, \quad (4)$$

422 where f_l is the fraction remaining liquid and α the fractionation factor.

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

$$f_l \equiv \frac{n_{w,1}}{n_{w,0}} = \frac{[\text{Cl}^-]_0}{[\text{Cl}^-]_1}. \quad (5)$$

426 By taking natural logarithms, one obtains:

$$\ln R_l \approx (1 - \alpha) \times \ln[\text{Cl}^-] + \epsilon, \quad (6)$$

427 As, by definition,

$$R_l \equiv R_{std.} \times \left(1 + \frac{\delta^{18}\text{O}}{1000}\right), \quad (7)$$

428 one has:

$$\ln R_l \equiv \ln R_{std.} + \ln\left(1 + \frac{\delta^{18}\text{O}}{1000}\right), \quad (8)$$

$$\approx \ln R_{std.} + \frac{\delta^{18}\text{O}}{1000}, \quad (9)$$

429 hence, with base 10 logarithms:

$$\delta^{18}\text{O} \approx 1000(1 - \alpha) \log[\text{Cl}^-] + \epsilon, \quad (10)$$

$$\approx -\epsilon \log[\text{Cl}^-] + \epsilon, \quad (11)$$

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

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

Locality	Lat.	Long.	Elev.	Date	/mS _m cm ⁻¹		pH	/mmolL ⁻¹									
					EC	T		Alk	Cl ⁻	SO ₄ ²⁻	Na ⁺	K ⁺	Mg ²⁺	Ca ²⁺	Br ⁻		
Hedbb I	3,534,750	723,986	134.8	09/11/2012	2.01	46.5	7.65	3.5	5.8	6.79	10.7	0.63	2.49	3.3			
Hedbb I	3,534,750	723,986	134.8	1992	1.9	49.3	7.35	0.42	5.81	1.07	5.71	0.18	0.77	0.48	0.034		
Hedbb II	3,534,310	724,290	146.2	1992	2.02	47.4	7.64	0.58	6.19	1.22	5.06	0.2	1.28	0.82			
Aoumet Mousa	3,548,896	721,076	132.6	1992	2.2	48.9	7.55	1.28	6.49	1.28	5.65	0.16	1.14	1.17			
Aoumet Mousa	3,548,896	721,076	132.6	22/02/2013	2.2	48.9	7.55	3.19	9.8	3.89	6.3	0.69	5.71	1.27			
Hedbb I	3,534,750	723,986	134.8	11/12/2010	2.19	49.3	7.35	1.91	12.4	4.58	10.7	0.7	3.77	2.35			
Hedbb II	3,534,310	724,290	146.2	1/12/2010	2.26	47.4	7.64	2.11	13.1	5.24	13.9	0.53	4.53	1.41			
Hedbb I	3,591,659	721,636	110	24/02/2013	2.43	50.5	6.83	2.98	14.3	5.24	10.8	0.84	3.44	4.63	0.033		
Hassi Khf	3,534,750	723,986	134.8	27/02/2013	2.01	46.5	7.65	3.46	15.1	7.67	11.8	0.51	5.57	5.16			
Hassi Khf	3,591,659	721,636	110	09/11/2012	2	50.1	7.56	3.31	15.3	7.77	12.2	0.59	5.77	4.95			
Hassi Khf	3,560,264	720,366	160	22/02/2013	2.96	54.5	7.34	2.58	18.6	6.21	20.6	0.66	4.79	1.38			

Table 6: Isotopic data ^{18}O and ^3H and chloride concentration in Continental Intercalaire, Complexe Terminal and Phreatic aquifers (sampling campaign in 1992).

Phreatic aquifer											
Piezometer	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT	Piezometer	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT	Piezometer	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT
P007	1.860.5	-2.49	0	PL15	23.54	-7.85	0.6(1)	P074	4.356.4	3.42	6.8(8)
P009	426.85	-6.6	1.2(3)	P066	80.23	-8.14	0.8(1)	PL06	14.15	-8.13	1.0(2)
P506	54.39	-6.83	1.6(3)	PL23	1,103.32	-6.1	0	PL30	24.32	-7.48	2.4(4)
P018	818.67	-2.95	6.2(11)	P063	1,379.3	-3.4	8.7(15)	P002	522.39	-5.71	0.6(1)
P019	779.13	-4.67	5.6(9)	P068	2,335.6	-3.04	8.8(14)	PL21	84.26	-7.65	1.2(2)
PZ12	2,405.5	-2.31	8.1(13)	P030	527.7	-6.57	2.4(4)	PL31	18.91	-7.38	1.6(3)
P023	1,176.9	-2.62	0.2(1)	P076	1,743.5	-5.56	2.8(5)	P433	12	-8.84	0
P416	2,433.7	-7.88	5.9(9)	P021	700.7	-5.16	2.6(4)	PL03	84.14	-7.35	1.7(3)
P034	2,752	-1.77	5.7(9)	PL04	716.27	-2.89		PL44	109.75	-8.82	1.0(2)
P036	4,972.7	3.33	2.1(4)	P093	2,198.5	-2.64	5.1(8)	PL05	30.87	-7.44	1.9(3)
P037	4,953.8	3.12	1.8(3)	P096	645.07	-6.13	4.8(8)	P408	24.16	-7.92	0
P039	4,189.5	0.97	2.2(4)	PLX1	1,296.6	-5.6	1.1(2)	PL16	31.94	-7.18	1.1(2)
P041	2,599.7	-0.58	7.3(13)	PLX2	25.68	-7.6	1.3(2)	LTP 16	213.35	-7.48	1.6(3)
P044	2,106.1	-4.46	2.7(5)	P015	134.68	-6.77	3.0(5)	PL17	32.81	-6.92	0.1
P014	336.96	-6.9	2.8(5)	P001	323.62	-4.66	2.5(4)	PL10	35.01	-7.31	0.2(1)
P012	539.3	-6.41	2.2(4)	P100	235.01	-5.81	0	PL25	75.57	-7.41	0.9(2)
P042	2,330.8	2.05	6.0(10)	P056	42.14	-7.03	2.9(5)	LTP30	18.21	-7.5	1.1(2)
P006	18.98	-6.64	0.5(1)	P113	954.89	-4.75	0.8(2)	LTP06	1,638.6	-1.97	2.8(5)
P057	28.21	-7.33	1.1(2)	PLX4	31.52	-7.1	0.3(1)	P031	481.83	-6.06	3.0(5)
P059	20.83	-7.81	0	P115	28.77	-2.54	6.8(12)				

Complexe Terminal aquifer											
Borehole	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT	Borehole	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT	Borehole	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT
D5F80	42.22	-7.85		D1F138	28.92	-8.13	0.7(1)	D2F71	13.53	-8.23	0.6(1)
D3F8	29.81	-8.14	1.4(2)	D3F18	21.66	-8.23	0.2(1)	D7F4	10.6	-8.27	0.1(1)
D3F26	34.68	-7.97	0.8(1)	D3F10	14.27	-7.88	1.5(2)	D2F66	11.02	-8.3	
D4F94	20.05	-8.18	0.6(1)	D6F51	28.39	-7.9	0.7(1)	D1F151	10.75	-8.32	0.4(1)
D6F67	18.79	-8.23	3.7(6)	D1F135	18.08	-7.97	1.1(2)	D6F64	11.36	-8.28	4.3(7)

Continental Intercalaire aquifer											
Borehole	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT	Borehole	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT	Borehole	Cl^- /mmol L $^{-1}$	$\delta^{18}\text{O}$ /‰	^3H /UT
Hadeb I	5.8	-8.02	0	Hadeb II	6.19	-7.93	0.1(1)	Aouinet Moussa	6.49	-7.88	1.1(2)

Table 7: Statistical parameters for Continental Intercalaire (CI), Complexe Terminal (CT) and Phreatic (Phr) aquifers samples selected on the basis of $\delta^{18}\text{O}$ and Cl^- data (see text).

Aquifer	Size	Parameter	EC /mS cm $^{-1}$	T /°C	pH	Alk.	Cl^-	SO_4^{2-}	Na^+	K^+	Mg^{2+}	Ca^{2+}
			/mmol/L									
CI	11	Average	2.2	49.0	7.5	2.3	11.0	4.7	10.3	0.51	3.6	2.4
CI	11	Stdd. dev.	0.3	2.0	0.2	1.0	4.6	2.5	4.6	0.23	2.0	1.8
CT	50	Average	3.2	23.0	7.8	2.3	20.0	8.9	17.0	1.0	5.5	5.6
CT	50	Stdd. dev.	1.1	2.4	0.4	0.8	7.0	2.6	6.0	0.8	2.2	1.7
Phr cluster I	30	Average	3.9	24.0	7.9	2.3	24.7	11.8	24.2	2.1	7.2	5.3
Phr cluster I	30	Stdd. dev.	1.3	1.3	0.4	1.0	6.9	3.4	11.0	1.7	5.0	2.7
Phr cluster II	3	Average		23.4	7.0	2.4	4,761.0	158.0	4,021.0	32.4	500.0	13.0
Phr cluster II	3	Stdd. dev.		0.1	0.5	1.6	350.0	43.0	1,093.0	28.0	378.0	8.0

Table 8: Summary of mass transfer for geochemical inverse modeling. Phases and thermodynamic database are from Phreeqc 3.0 (Parkhurst and Appelo, 2013).

Phases	Stoichiometry	CI/CT	CT/Phr I	Rainwater/P036	PhrI/PhrII 60%/40%
Calcite	CaCO ₃	—	-6.62×10^{-6}	-1.88×10^{-1}	-2.26×10^{-1}
CO ₂ (g)	CO ₂	-6.88×10^{-5}	—	8.42×10^{-4}	5.77×10^{-4}
Gypsum	CaSO ₄ · 2 H ₂ O	4.33×10^{-3}	—	1.55×10^{-1}	1.67×10^{-1}
Halite	NaCl	7.05×10^{-3}	3.76×10^{-3}	6.72	1.28
Sylvite	KCl	2.18×10^{-3}	1.08×10^{-3}	4.02×10^{-1}	—
Bloedite	Na ₂ Mg(SO ₄) ₂ · 4 H ₂ O	—	1.44×10^{-3}	—	—
Huntite	CaMg ₃ (CO ₃) ₄	—	—	4.74×10^{-2}	5.65×10^{-2}
Ca ion exchange	CaX ₂	-1.11×10^{-3}	—	—	—
Mg ion exchange	MgX ₂	1.96×10^{-3}	—	1.75×10^{-1}	-2.02×10^{-1}
Na ion exchange	NaX	—	—	—	3.92×10^{-1}
K ion exchange	KX	-1.69×10^{-3}	—	-3.49×10^{-1}	1.20×10^{-2}

Values are in mol/kg (H₂O). Positive (mass entering solution) and negative (mass leaving solution) phase mole transfers indicate dissolution and precipitation, respectively; — indicates no mass transfer.

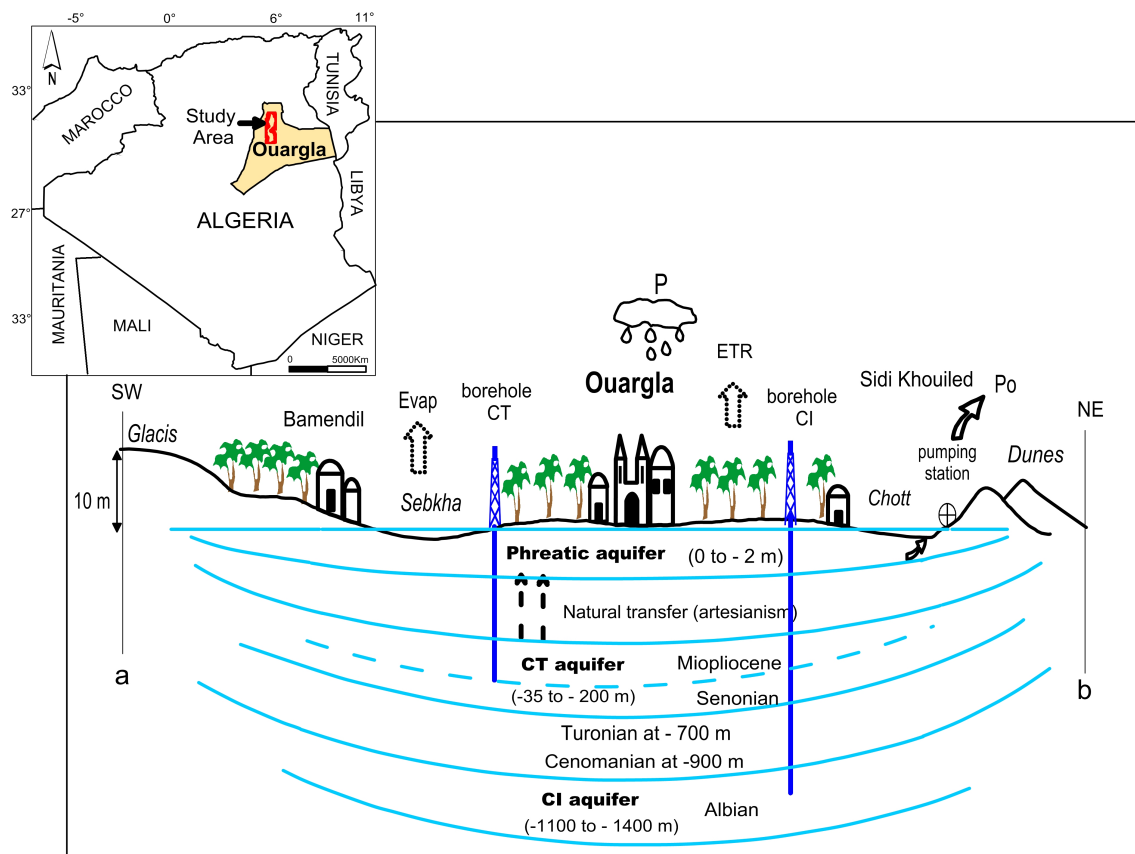


Figure 1: Localisation and schematic relations of aquifers in Ouargla. *Blue lines represent limits between aquifers, and the names of aquifers are given in bold letters; as the limit between Senonian and Mio-pliocene aquifers is not well defined, a dashed blue line is used. Names of villages and cities are given in roman (Bamendil, Ouargla, Sidi Khouiled), while geological/geomorphological features are in italic (Glacis, Sebkh, 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).*

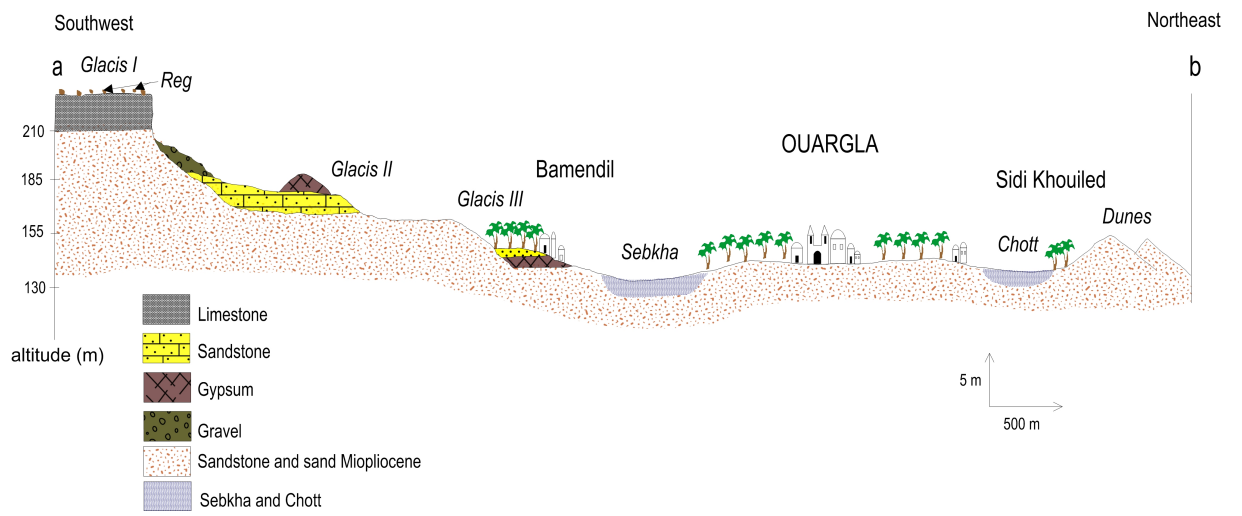


Figure 2: Geologic cross section in the region of Ouargla.
The blue pattern used for Chott and Sebka correspond to the limit of the saturated zone.

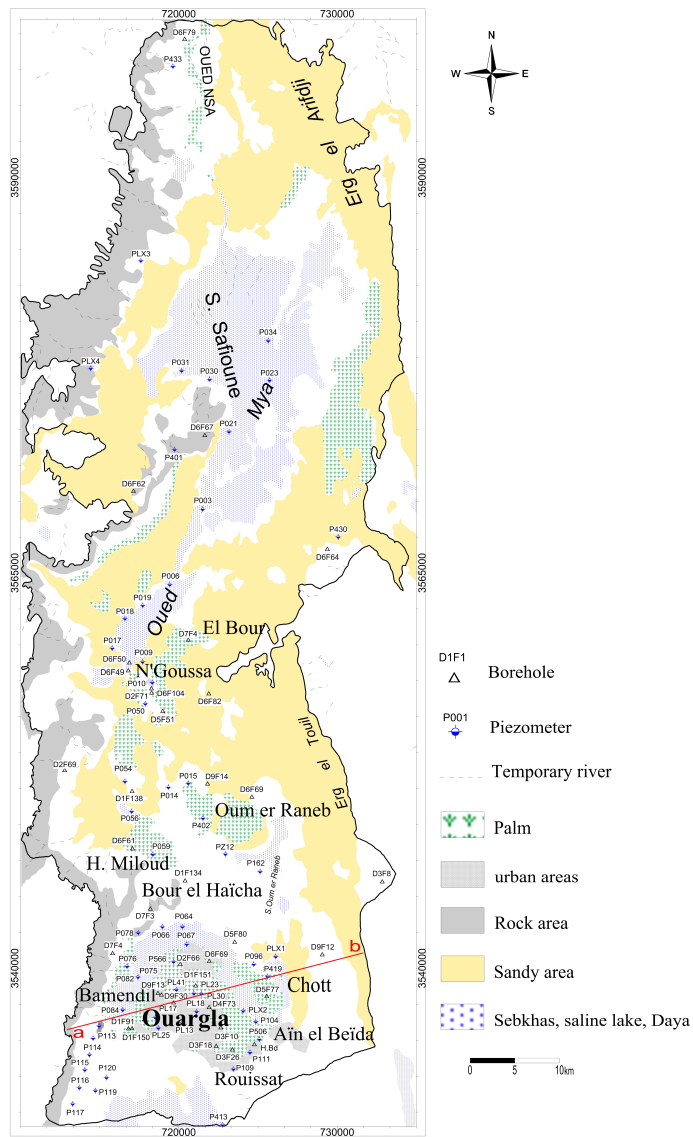


Figure 3: Localisation map of sampling point

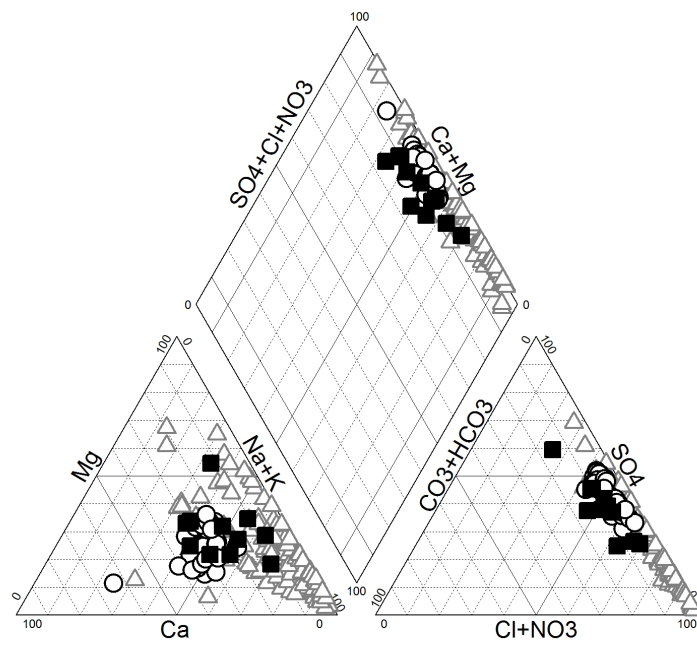
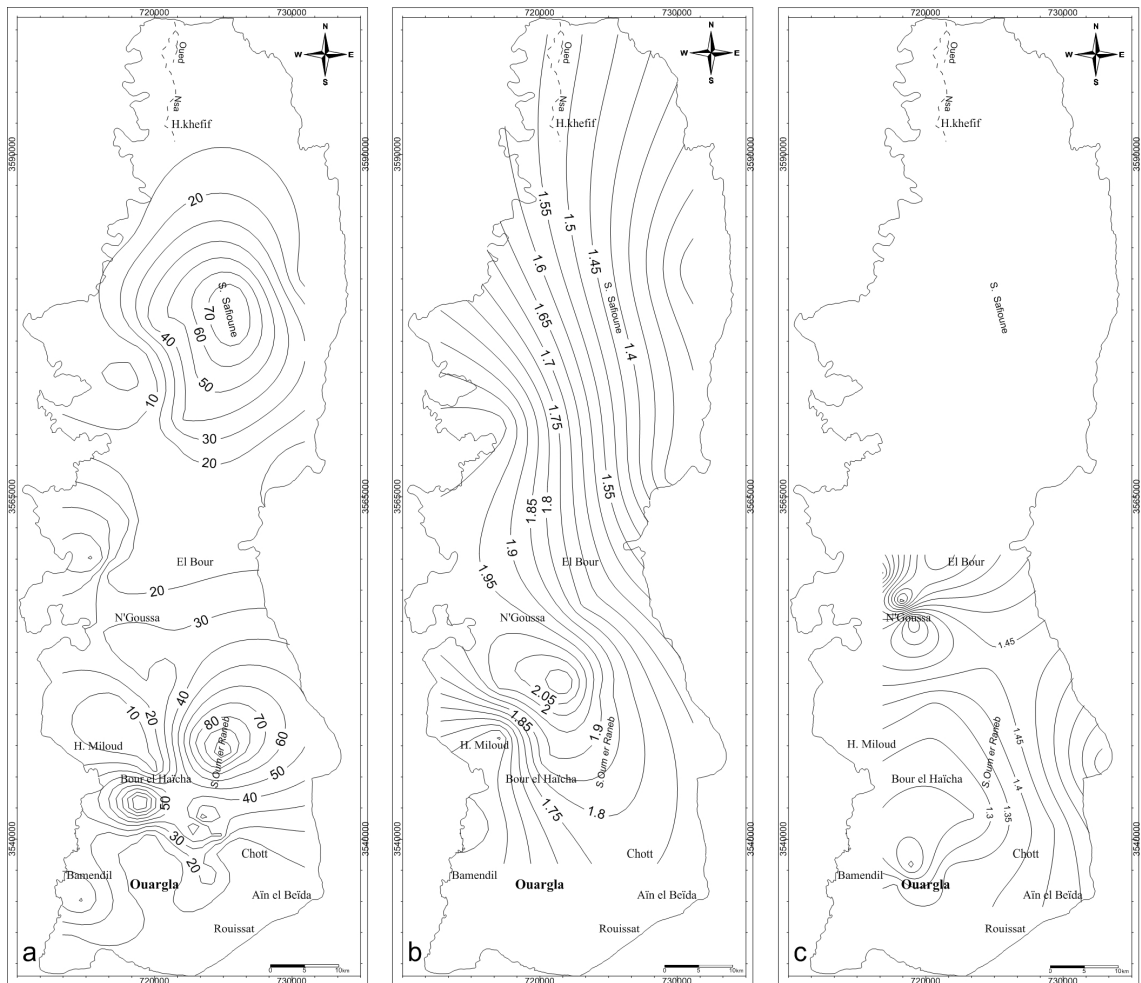


Figure 4: Piper diagram for Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles).



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Figure 5: Contour maps of the salinity (expressed as global mineralization) in the aquifer system, (a) Phreatic aquifer; (b) and (c) Complex Terminal [(b) Mio-pliocene and (c) Senonian]; figures are isovalues of global mineralization (values in g/L).

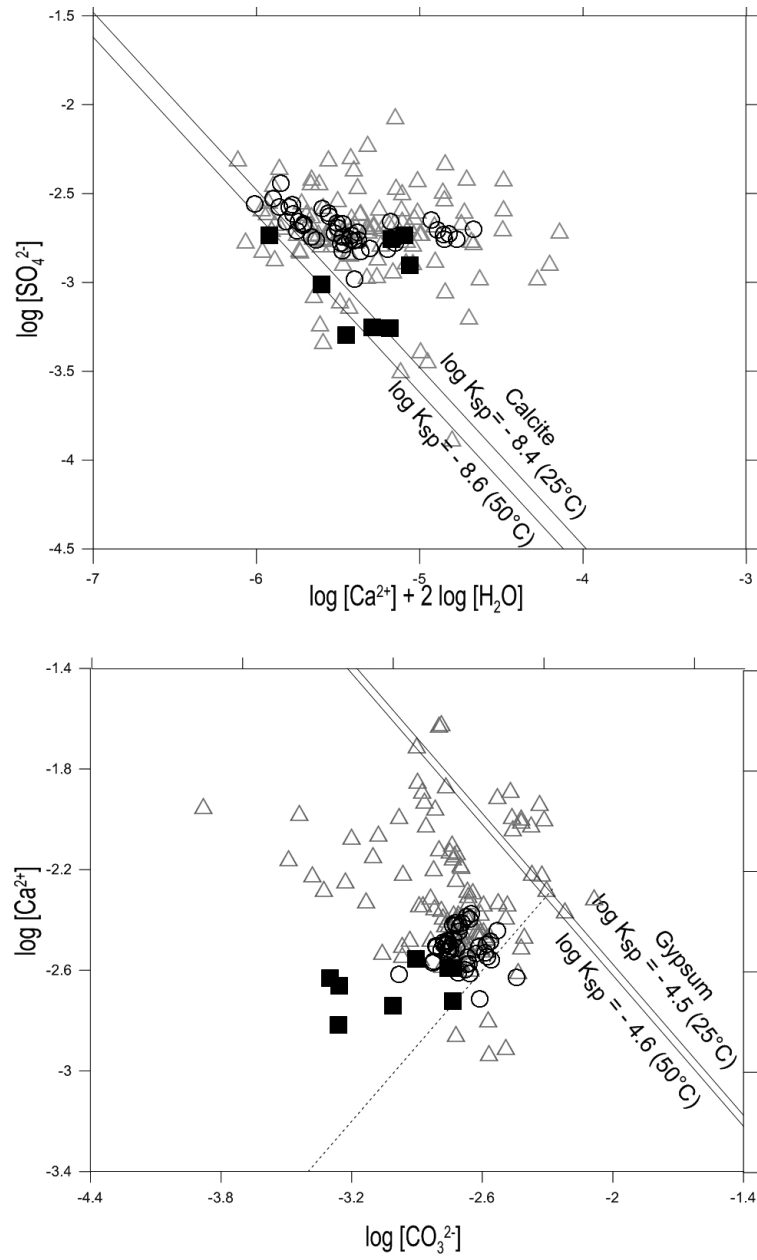


Figure 6: Equilibrium diagrams of calcite (top) and gypsum (bottom) for Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles). Equilibrium lines are defined as: $\log[\text{Ca}^{2+}] + \log[\text{CO}_3^{2-}] = \log K_{sp}$ for calcite, and $\log[\text{Ca}^{2+}] + 2 \log[\text{H}_2\text{O}] + \log[\text{SO}_4^{2-}] = \log K_{sp}$ for gypsum.

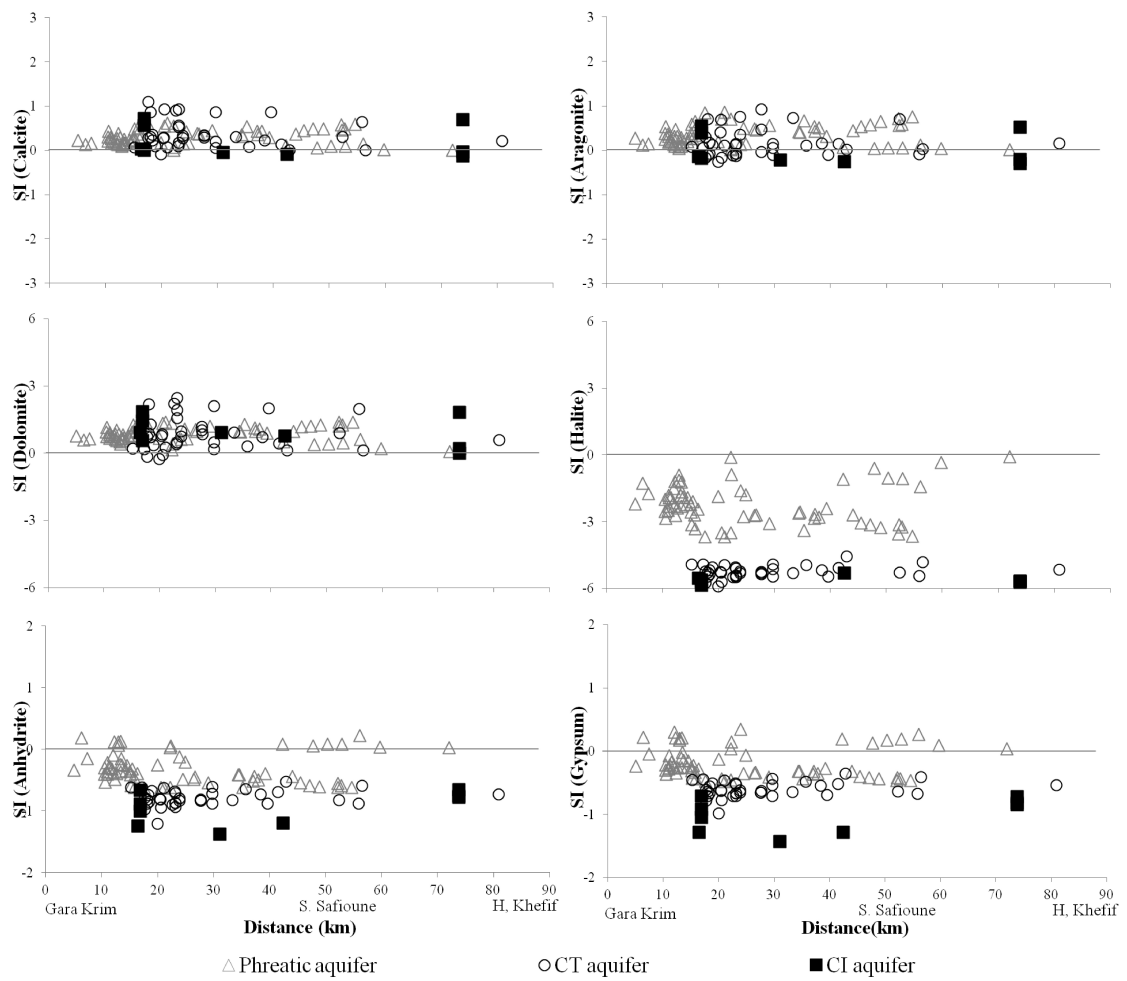


Figure 7: Variation of saturation indices with distance from south to north in the region of Ouargla.

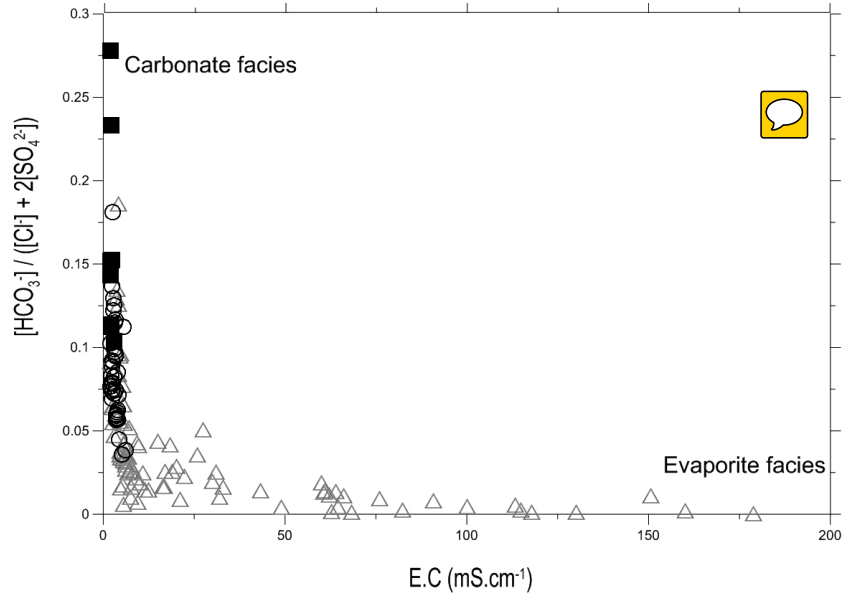


Figure 8: Change from carbonate facies to evaporite from Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles).

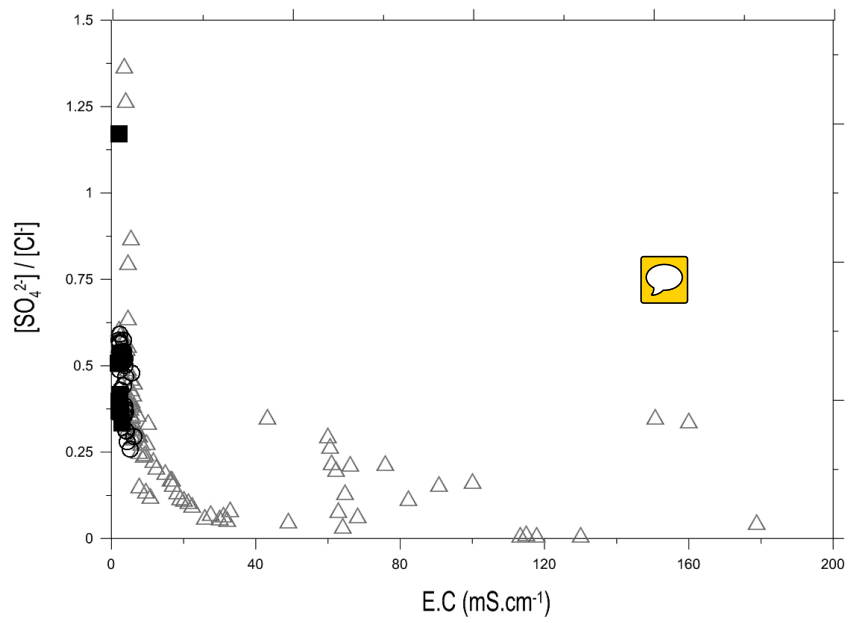


Figure 9: Change from sulfate facies to chloride from Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles).

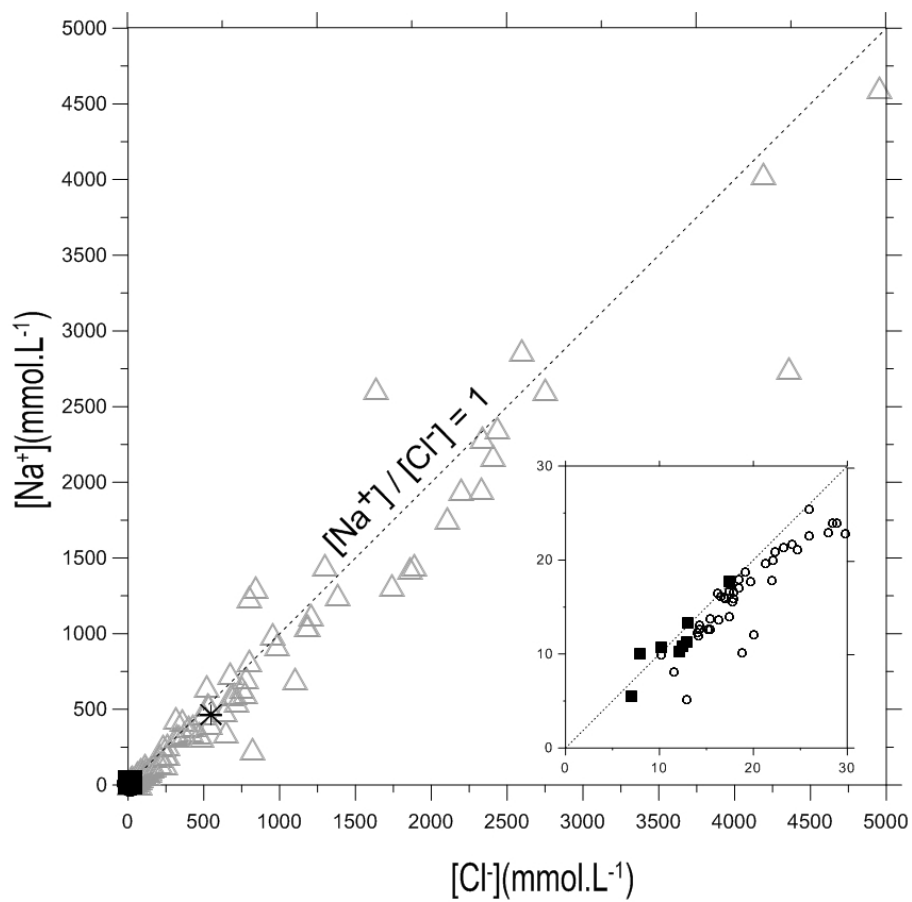


Figure 10: Correlation between Na^+ and Cl^- concentrations in Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles). Seawater composition (star) is $[Na^+] = 459.3$ mmol L⁻¹ and $[Cl^-] = 535.3$ mmol L⁻¹ (Stumm and Morgan, 1999, p.899).

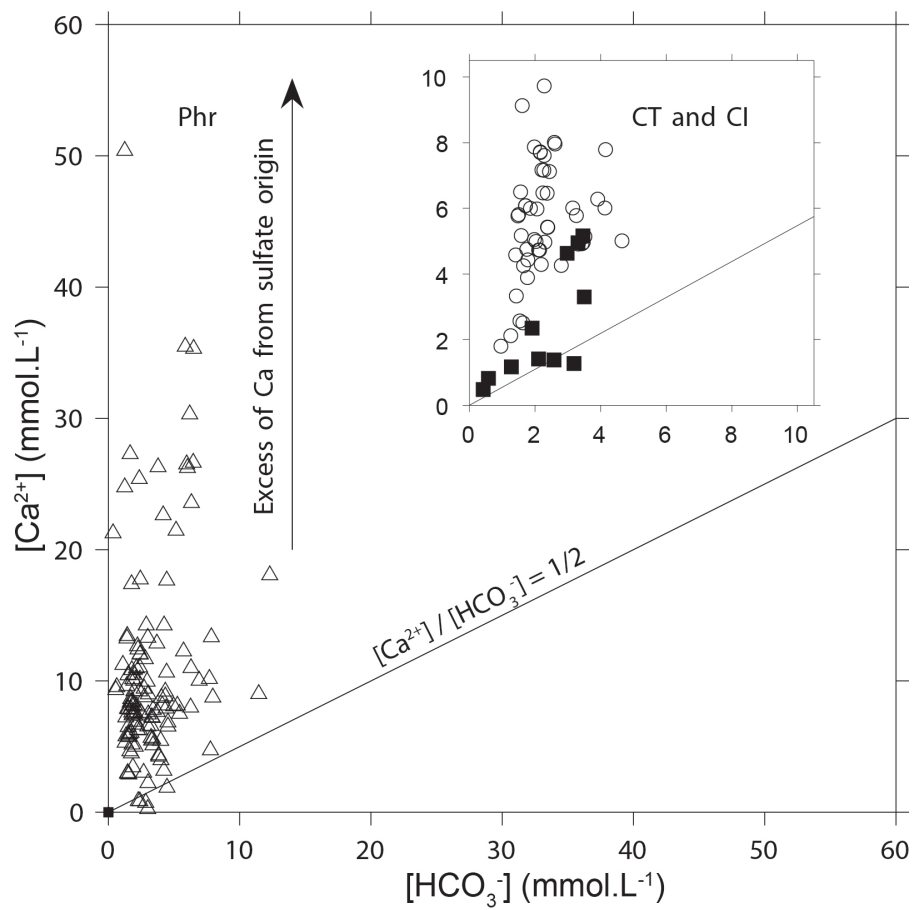


Figure 11: Calcium vs. HCO_3^- diagram in Continental Intercalaire (filled squares), Complexe Terminal (open circles), Phreatic aquifer (open triangles) and Seawater composition (star) is $[Ca^{2+}] = 10.2 \text{ mmol.L}^{-1}$ and $[HCO_3^-] = 2.38 \text{ mmol.L}^{-1}$ (Stumm and Morgan, 1999, p.899).

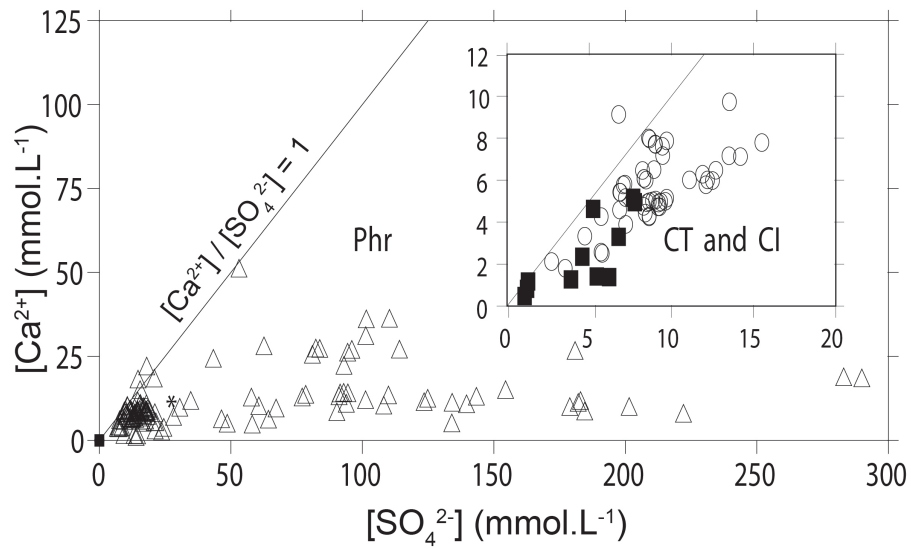


Figure 12: Calcium vs. SO_4^{2-} diagram in Continental Intercalaire (filled squares), Complexe Terminal (open circles), Phreatic aquifer (open triangles) and Seawater composition (star) is $[\text{Ca}^{2+}] = 10.2 \text{ mmol L}^{-1}$ and $[\text{SO}_4^{2-}] = 28.2 \text{ mmol L}^{-1}$ (Stumm and Morgan, 1999, p.899).

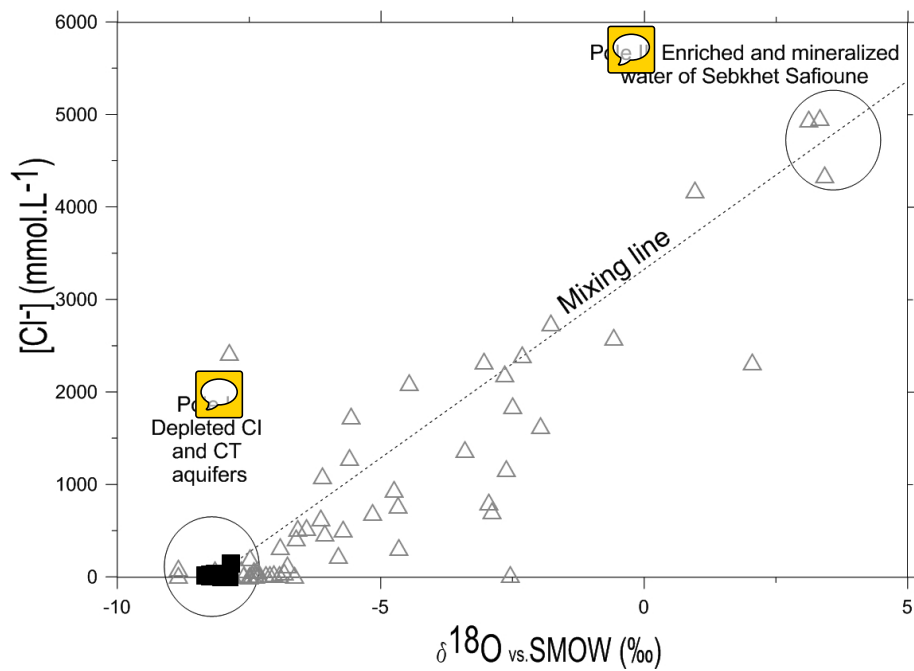


Figure 13: Chloride concentration versus $\delta^{18}\text{O}$ in Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles) from Ouargla.

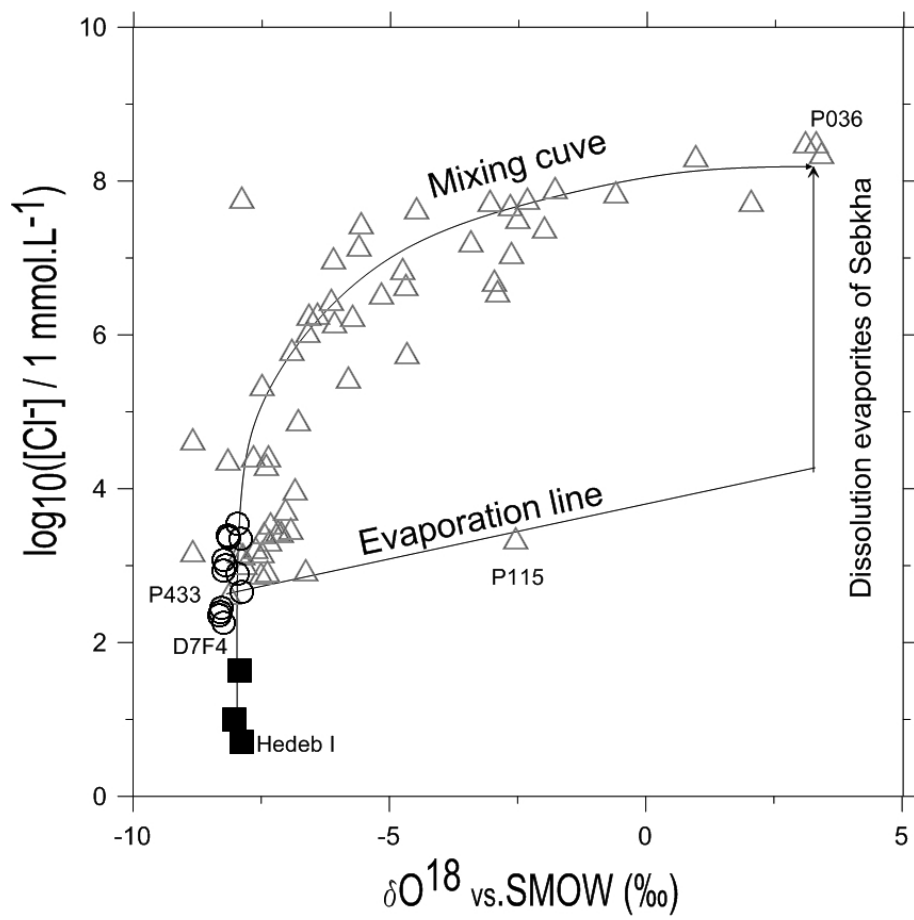


Figure 14: Log $[\text{Cl}^-]$ concentration versus $\delta^{18}\text{O}$ in Continental Intercalaire (filled squares), Complexe Terminal (open circles) and Phreatic aquifer (open triangles) from Ouargla.

Dear editor,

The following modifications have been made:

1- The address has been modified

- Line 4 : ^aUniv Ouargla, Fac. des sciences....
- ^aOuargla University, Fac. des Sciences de la Nature et de la Vie, Lab. Biochimie des Milieux Désertiques, Ouargla 30000, Algeria.

2- The address has been modified

- Line 8 : ^dNuclear Research Centre....
- ^dAlgiers Nuclear Research Centre, P.O. Box, 399 Alger-RP, 16000 Algiers, Algeria.

3- The abstract has been modified accordingly

- Line 10 : New samples....
- 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 a Saharan aquifer system and investigate the processes through which groundwaters acquire their mineralization.

4- What do you mean pole?

- Line 17 : ...a first pole of Phr....
- The pole mean «end member, cluster»

5- The Reference added

- Line 25 : A scientific study...
- A scientific study published in 2008 (OECD, 2008).

6- It has been replaced

- Line 29 : ...causing most of the time overuse...
- often causing overuse.

7- It has been replaced

- Line 33 : ... is almost unexploited (only north of Ouargla) due...
- is almost unexploited, due to its salinity (50 g/L);

8- It has been deleted

- Line 34 : ... "Complexe Terminal" (CT) aquifer,...
- in the middle, the "Complexe Terminal" (CT)

9- It has been deleted

- Line 35 : ...which is the most exploited, and includes...
- is the most exploited and includes

10- It has been replaced

- Line 37 : ...Miopliocene...

– Mio-pliocene

11- It has been replaced

- Line 37 : ...“Continental Intercalaire” (CI) aquifer, where water is contained in...

– at the bottom, the “Continental Intercalaire” (CI), hosted in the lower Cretaceous

12- it has been rephrased

- Line 46 : tried, starting fromContinental Intercalaire recharge.

– started from chemical and isotopic information (^2H , ^{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.

13- Stress the scientific novelty of this paper. From this description it seems that nothing really new is proposed from the scientific point of view, but one of the referees stressed the importance of reducing the lack of data for African regions. I think you can reinforce both the methodological aspects (which is the open scientific question? How is it faced in this work?) and the "geographical" application.

- Line 53 : In the present study...

– The present study aims at applying for the first time ever in Algeria, a new methodology (inverse modeling) to an extreme environment where lack of data on a scarce natural resource (groundwater) is observed. 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.

14- The word has been replaced

- Line 56 : ...simulations...

– ...modeling...

15- it is now explained

- Line 60 : The stepwise...

– The stepwise inversion strategy involves designing a list of the scenarios that includes the most plausible combinations of geochemical processes, solving scenarios in a stepwise manner, and selecting the scenario that provides the best conceptual geochemical model.

16- It has been deleted

- Line 69 : the quaternary fossil valley of Oued Mya basin

– It is located in the quaternary valley of Oued Mya basin.

17- The sentences have been modified and completed

- Line 75 : During Secondary era...

– 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), an epicontinental sea spread to the Lower Eocene of northern Sahara. After the Oligocene, the sea gradually withdrew.

18- It has been rephrased

- Line 100 : The sampling scheme...
- The sampling scheme complies with the flow directions of the two formations (Phr and CT aquifers); for the CI aquifer only five points are available, so it is impossible to choose a transect (Fig. 3). Groundwater samples (n = 107) were collected during a field campaign in 2013, along the main flow line of Oued Mya, 67 piezometers tap the phreatic aquifer, 32 wells tap the CT aquifer and 8 boreholes tap the CI aquifer (Fig. 3).

19- The Reference added

- Line 112 : Scatchard and Guggenheim....
- 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).

20- The whole paragraph has been modified

- Line 119 : The Inverse modeling.....
- 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.

21- It has been rephrased

- Line 129 : Samples are...
- 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.

22- It has been rephrased

- Line 141 : The facies of the Phreatic aquifer ...
- Respectively, CaSO_4 , Na_2SO_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 Melrhir.

23- It has been replaced

- Line 148 : The salinity of the phreatic aquifer...

- 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).

24- It has been rephrased

- Line 157 : The salinity of the Complexe Terminal...
- 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;

25- It has been rephrased

- Line 177 : No significant...
- No significant saturation indices' evolution from the south to the north upstream and downstream of Oued Mya.

26- It has been rephrased

- Line 193 : For most of the sampled...
- $[Na^+]/[Cl]$ ratio is from 0:85 to 1:26 for CI aquifer, from 0:40 to 1:02 for the CT aquifer and from 0:13 to 2:15 for the Phr aquifer.

27- I wonder whether it could be useful to add this line to the plots of figure 10

- Line 202 : ...the seawater mole ratio (0,858), ...
- There is a star * in the plot, and the values are given in the caption of figure 10, but the values are very close to the 1:1 line and masked by samples.

28- It has been rephrased

- Line 209 : In these aquifers,...
- 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 $[Ca^{2+}]/[HCO_3^-]$ 1:2 line, while calcium sulfate dissolution explains the excess of calcium. However, nine samples from phreatic aquifer are depleted in calcium, and plot under the $[Ca^{2+}]/[HCO_3^-]$ 1:2 line.

29- Recall whether this linement has a geological or hydrogeological importance.

- Line 227 : Waters located north of the Hassi Miloud to Sebket Safioune axis are more enriched in heavy isotopes and therefore more evaporated.
- This is not a linement of hydrogeological importance, but results from anthropogenic influence by irrigation. Far from Ouargla, there is no irrigation, while in the vicinity of Ouargla, irrigation waters are directly pumped in the CI and mostly CT aquifers, so these irrigation waters both evaporate and mix with Phr waters.

30- Symbol changed to constant

- Line 249 : Equation 1

31- It has been rephrased and the order of sentences modified

- Line 254 : There is only one sample...

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.

32- Equation 3 has been changed

- Line 266 : $\delta_{\text{mix}} = f_1 \times \delta_1 + f_2 \times \delta_2$
- $\delta_{\text{mix}} = f_1 \times \delta_1 + (f_1 - 1) \times \delta_2$

33- It has been rephrased

- Line 296 : This values are dated...
- 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.

34- It has been rephrased.

- Line 290 : The comparison of these...
- 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.

35- The whole paragraph has been modified

- Line 292 : This value seems...
- 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.

36- It has been rephrased.

- Line 354 : In a decreasing order ...
- In a descending order of amount, halite, sylvite, gypsum and huntite are the minerals that are the most involved in the dissolution process.

37- Reference added in the tables

- Tableau : In these tables, provide information about the reference system for Latitude and Longitude. Moreover, some data are given with decimal digits. Is this physically significant?
- The reference is UTM 31 projection for North Sahara 1959 (CLARKE 1880 ellipsoid). The decimal digits are not physically significant, and simply indicative to locate sampling sites.

Best regards

Slimani Rabia