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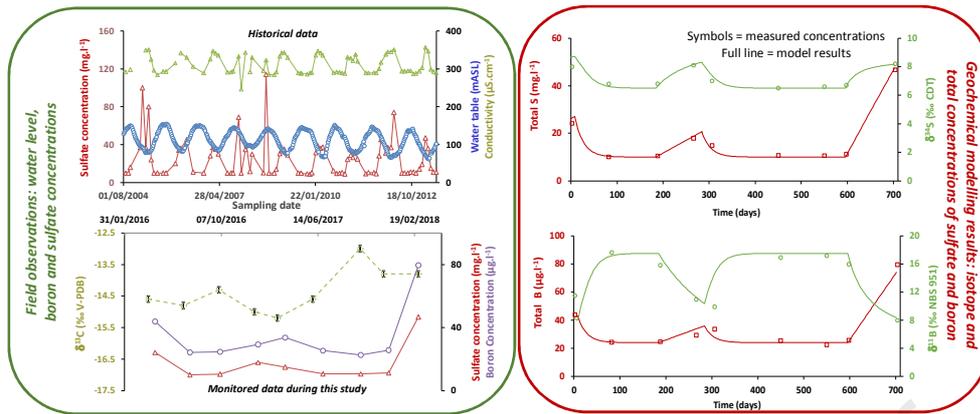
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## Graphical abstract



1  
2 Cyclic variations of sulfate and boron concentrations and  
3 isotopes in deep groundwaters in the Aquitaine Basin,  
4 France

5  
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27

28 **Abstract**

29 Concentrations and isotope contents of major and trace elements are principal factors in  
30 determining the origin of the chemical composition of groundwater. This paper focuses  
31 specifically on the use of sulfur and boron isotopes to characterize the origin of cyclic variations  
32 in the deep Eocene aquifer in the Aquitaine sedimentary basin (southwest of France). It is part  
33 of a multi-layer system mainly composed of sands and sandstone deposits. Groundwater  
34 contained in this deep reservoir is known to present stable chemical compositions, allowing its  
35 use for various purposes like drinking water, geothermal energy, thermal activity and agricultural  
36 irrigation. However, among the dozens of wells exploiting this aquifer and despite the reservoir's  
37 substantial depth, variations in sulfate concentration have been identified in a limited area of the  
38 reservoir. These fluctuations are cyclic and they seem to be correlated with water level  
39 variations due to gas storage activities nearby in the same aquifer. Regular water samplings  
40 and analyses of major and trace elements and their isotopes have identified that bore  
41 concentration variations are correlated with sulfate variations. A geochemical modelling  
42 approach based on water mixes elucidates the causes of these variations in chemical  
43 composition, especially the boron and sulfate concentrations and their respective  $\delta^{11}\text{B}$  and  
44  $\delta^{34}\text{S}_{\text{SO}_4}$  values. From these numerical results, we identify that different sources explain the  
45 variations of boron concentration, one part coming from the silicates alteration (present in sub-  
46 layers of the exploited aquifer) and the other part coming from the evaporites alteration (present  
47 in the underlying molasse unit). These results also confirm the existence of mass and potentially  
48 water transfers between the different sub-layers of the reservoir and with the underlying  
49 molasse aquitard, implying new constraints for the future hydrogeologic modelling.

50 **Keywords:** deep aquifer; France; groundwater; sulfur stable isotopes; boron stable isotopes;  
51 mixing geochemical models.

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## 55 **1 - Introduction**

56 The Aquitaine basin is a wide sedimentary basin located in the southwest of France. It is  
57 constituted of aquitards and aquifers used for different purposes. Because of the various uses  
58 of the aquifers, the aquifer needs to be efficiently managed and the resources have to be  
59 investigated. To achieve this, public and private institutions initiated recent investigations on the  
60 Eocene aquifer through a scientific project named GAIA (Wuilleumier et al., 2018). This study  
61 embraces numerous areas of the earth sciences, including geology (Ortega et al., 2017),  
62 hydrogeology and hydrogeochemistry (Wuilleumier et al., 2018; Gal et al., 2018 a,b; André et  
63 al., 2018).

64 For the hydrogeochemistry research, the main goal is to investigate in detail the origin of water  
65 mineralization. The water chemistry in the Eocene aquifer (Aquitaine Basin – Southwest of  
66 France - Figure 1) has been investigated through different studies. Blavoux et al. (1993) were  
67 the first to investigate the isotope composition of the Eocene reservoir waters with  
68 characterization of  $^2\text{H}$ ,  $^{18}\text{O}$ , tritium, noble gases and carbon-14 activity. They defined that waters  
69 have a meteoric origin with a late Pleistocene origin. The authors concluded their article that the  
70 reservoir is a complex system and they did not exclude a recharge through the overlying  
71 molassic unit. They also supposed that additional investigations on sulphur components  
72 (including isotopes) could bring information on the origins for water mineralization. In agreement  
73 with these conclusions, isotopic analyses have helped to identify geochemical basins whose  
74 properties modify the chemical water composition (André, 2002; André et al., 2002; Douez,  
75 2007). These studies showed that the  $\delta^{34}\text{S}$  of gypsum sampled in the molasse unit was  
76 consistent with  $\delta^{34}\text{S}$  values of dissolved sulfate in the reservoir waters. The study confirms the  
77 hypothesis of Blavoux et al. (1993) on the potential transfers between the molassic aquitard and  
78 the reservoir. Hydrogeochemical investigations continued with the CARISMEAU project (Négre  
79 et al., 2007; 2009). During this study, the  $\delta^{34}\text{S}$  of sulfate was also investigated in the Northern  
80 part of the reservoir (Entre-deux-mers area), coupled with other parameters like  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio  
81 (Brenot et al., 2015) or with fluoride measurements (Malcuit et al., 2014) to investigate the  
82 mineralization origin of waters. However, despite these investigations, some mechanisms are  
83 still unknown. Indeed, all the previous chemical investigations showed that the chemical  
84 composition of waters from this deep aquifer (about 500–1000 m depth) does not change  
85 usually with time. However, seasonal variations in sulfate concentrations occur in a specific area  
86 of the aquifer (Nogaro 2 well – Figure 2). About 200 samples collected at this well over more  
87 than 20 years show variations between 10 and about 100  $\text{mg SO}_4\cdot\text{l}^{-1}$  (sometimes higher). These  
88 varied sulfate concentrations are correlated with the water conductivity and anti-correlated with

89 piezometric variations (reaching about 80 m per year), which are due to the impact of gas  
90 storage activities occurring within the same aquifer.

91 During this study, additional hydrogeochemical monitoring was implemented for two years to  
92 increase our understanding of the mechanisms underlying these sulfate fluctuations. We  
93 focused on how sulfate concentration changed over time but also investigated the other major  
94 elements, traces and isotopes in the waters of the Nogaro 2 well, which exploits the Eocene  
95 aquifer. The Nogaro 2 well (reference: BSS002EFSB - see Infoterre, 2020a) is used to supply  
96 drinking water to the city of Nogaro (Gers Department). It was drilled in 1982 and has been  
97 monitored regularly for chemical composition of groundwater. Two other wells located  
98 respectively 12 and 15 km from the Nogaro 2 well, were also monitored over the same period in  
99 order to compare the potential seasonal variations in the waters' chemical composition. Also  
100 used for drinking water supply, the Eauze well (reference: BSS002EGAG - see Infoterre, 2020b)  
101 and the Dému well (reference: BSS002EFZJ - see Infoterre, 2020c) pump within the same  
102 aquifer and are also influenced by the hydrogeologic conditions of this zone.

103 Chemical analyses focused on major and trace elements but also stable and radioactive  
104 isotopes. In coherence with former analyses, the new investigations confirm the sulfate  
105 variations (both total sulfur and  $^{34}\text{S}$  concentration). Isotopes of dissolved sulfate are widely used  
106 in large basins worldwide for identifying sulfur origins in water (De Caritat et al., 2005; Li et al.,  
107 2011; Einsiedl et al., 2015).  $^{34}\text{S}$  in sulfate is a geochemical tracer for obtaining information on  
108 the origin of sulfur and biological processes that may alter sulfate compositions in water (such  
109 as bio-sulfate-reduction). As part of this study, this isotope was tracked over time to better  
110 understand the origin of sulfate variations (André et al., 2002; Négrel et al., 2009). The new  
111 analyses on Nogaro 2 has also revealed remarkable boron variations (both total boron and  $^{11}\text{B}$   
112 content) correlated with sulfur variations.  $^{11}\text{B}$  is a tracer used to define the origin of boron in  
113 solution, mainly the characterization of water/rock interactions in sedimentary basins (Négrel et  
114 al., 2012; Deiana et al., 2020), weathering processes in surface and subsurface systems  
115 (Lemarchand and Gaillardet, 2006; Ercolani et al., 2019), pollution sources and/or the anthropic  
116 inputs (Harkness et al., 2018) and salinization of coastal aquifers (Cary et al., 2015). The  $\delta^{11}\text{B}$   
117 value is also impacted by adsorption processes with a preferred adsorption of the light isotope  
118 ( $^{10}\text{B}$ ) and an enrichment of the solution in heavy isotope  $^{11}\text{B}$  (Palmer et al., 1987; Godfrey and  
119 Alvarez-Almado, 2020). At last, carbon-13 is a geochemical marker of water-rock interactions  
120 (including carbonates) and carbon-14 activity is used as an indicator of the apparent age of  
121 water.

122 Our goal in this paper was to document the mechanisms controlling the variations in chemical  
123 composition in the groundwater in this specific area and to identify potential causes of these  
124 cyclic disturbances. After interpreting the chemical analyses, we carried out geochemical  
125 modelling to characterize, from a mixing model, the different end-members (waters of different  
126 horizons) that could be responsible for these concentration variations.

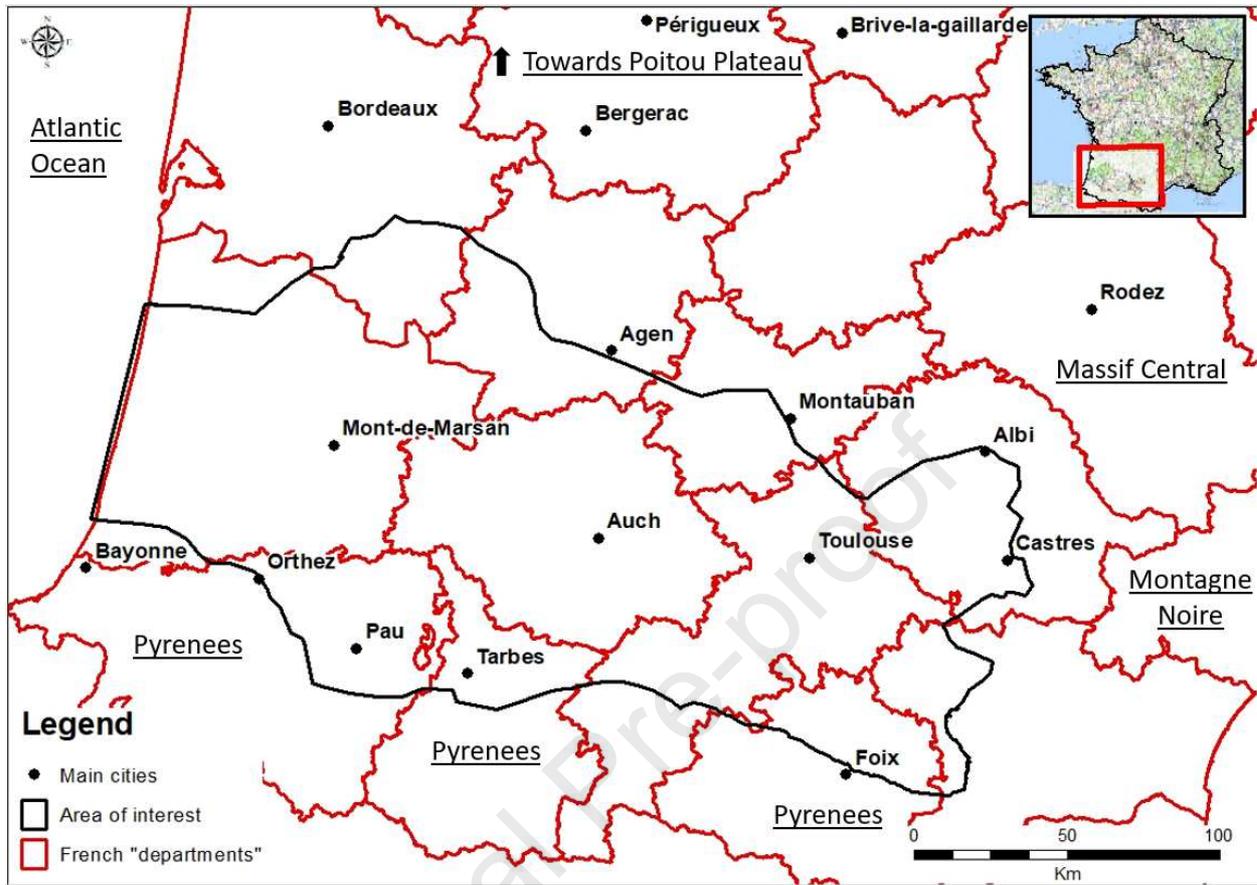
## 127 **2 – Geology, mineralogy and hydrogeological settings**

### 128 **2.1 - Geology**

129 The Aquitaine Basin is a large sedimentary basin limited in the east by the foothills of Montagne  
130 Noire, in the south by the North Pyrenean Piedmont, in the west by the Atlantic Ocean and in  
131 the north by the Poitou Plateau (Figure 1).

132 The area is characterized by a thick layer of detritic deposits (molasse) aging from late Eocene  
133 to Miocene (Figure 2) and originating from the surrounding landforms (Massif Central, the  
134 Montagne Noire and the Pyrenees mountains). This deposit starts at the beginning of the  
135 Priabonian, when a drop in sea level led to a progression of late orogenic continental molassic  
136 sediments (Orthiz, 2019). The development of the Campagne formation, mainly marly,  
137 corresponds to a general regression and thus mark the continentalization of most of the Adour  
138 basin, a sub-basin located in the southwest of Aquitaine Basin (Serrano, 2001). The lake and  
139 river facies of these continental deposits have many evaporitic levels and numerous gypsum  
140 indices were found in the Campagne formation (Priabonien).

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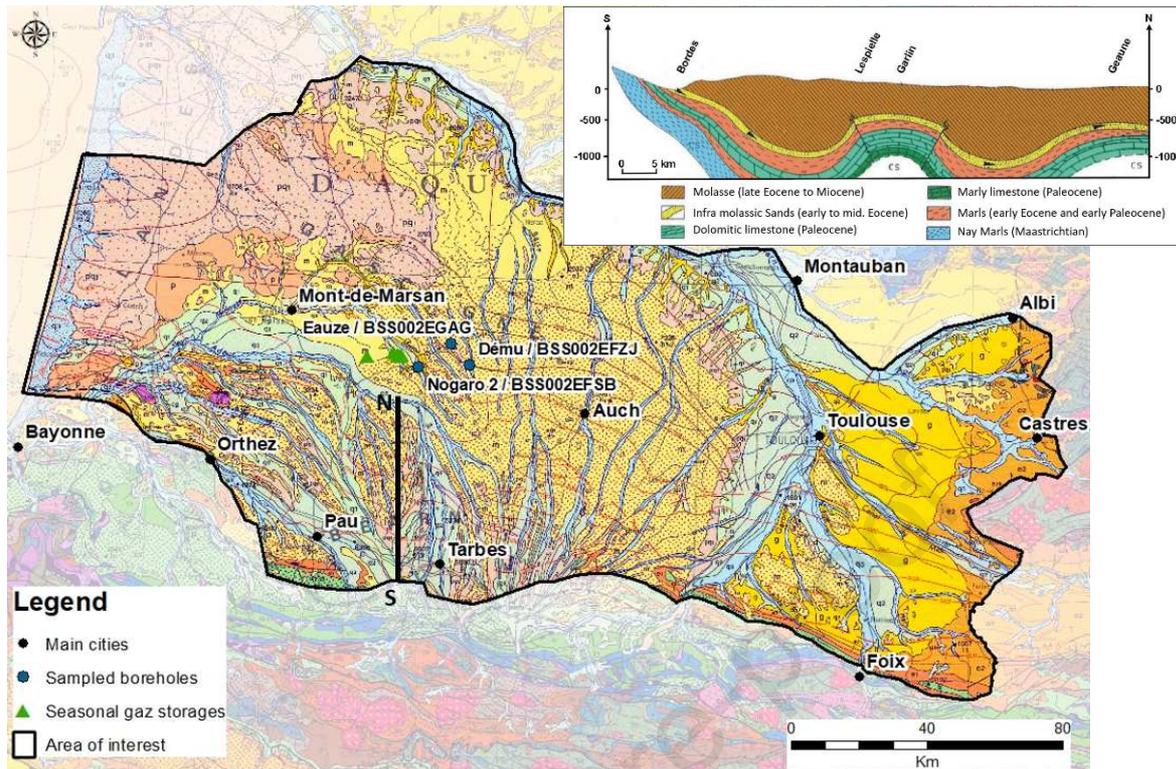
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143 **Figure 1 – Location map. The area of interest corresponds to the region investigated in**  
 144 **the GAIA Project.**

145 This formation overlies (Douez, 2007) the so-called Infra-Molassic Sands (SIM) of the early to  
 146 mid-Eocene (Figure 2), which is mostly consisting of the Lussagnet sands of the Cuisian to  
 147 Lutetian age, a prograding deltaic formation, and the underlying Nummulites sandstone of the  
 148 Ypresien age, integrated into the Baliros sands formation. That sandy Eocene formation lies  
 149 generally upon a layer of marl and clay deposits of the early Eocene and late Paleocene, which  
 150 thickness usually ranges from 100 to some hundreds of meters (Beicip, 1984; Angrand, 2017),  
 151 but, according to the location in the basin, it can lie directly upon the limestone and dolomitic  
 152 limestone of the Paleocene (Douez, 2007).

153

154



155  
 156 **Figure 2 – Geological map (to 1 million) of the area and location of the three sampled**  
 157 **wells: Nogaro 2, Eauze and Dému. Black line NS is a geological South-North schematic**  
 158 **cross-section (adapted from Douez, 2007).**

159 The depth of the top of the Eocene sand layer shows notable variations according to the  
 160 location in the basin. The Nogaro 2 well corresponds to a low point with a depth of about 920 m.  
 161 The depth of the sand layer varies for many reasons. First, the thicknesses of the deposits may  
 162 differ from one point to another in the sector depending on the amount of sediment stored  
 163 during the progradation of the fan delta westward during the Middle Eocene, i.e. during the  
 164 maximum peak of the Pyrenean compression, which corresponded to the maximum sediment  
 165 discharge. In this type of context, the rate of movement of the delta position and the amount of  
 166 detritus can change. Second, a massive but heterogeneous subsidence impacted the entire  
 167 basin during the Pyrenean orogeny. During the Pyrenean compression responsible for this  
 168 subsidence, the propagation of tectonic stresses also generated significant deformations in the  
 169 South Aquitaine basin. At the origin of a “piercing” diapirism (particularly in the western part of  
 170 the basin: Dax, Tercis, Bastenne-Gaujac, etc.) or of a “blind” diapirism (like in Audignon, Lacq,  
 171 Meillon), these long wavelength deformations affect part of the tertiary deposits, in particular by  
 172 installing anticline structures (Bourrouilh et al., 1995; Serrano, 2001; AGSO and BRGM, 2018).

## 173 2.2 - Hydrogeology

174 The Eocene aquifer is a major aquifer in the Aquitaine sedimentary basin and it is used for uses  
175 such as drinking water, field irrigation, thermalism and spas, gas storage and as a thermal  
176 resource. This aquifer extends over 150 km from east to west and 200 km from south to north  
177 and constitutes a part of a multi-layer system. The Eocene sands aquifer is covered by several  
178 hundreds of meters of Tertiary molasse unit of low permeability. Therefore, the Eocene aquifer  
179 is confined over the studied area. Part of its outcrops are located in the South, close to the  
180 Pyrenees Mountains, and in the East, in the Montagne Noire region (Figure 1). At least, the  
181 mean annual air temperature at Mont-de-Marsan is 13.6°C for the 1981-2010 period  
182 (MeteoFrance, 2020).

183 The average thickness of the Eocene aquifer varies according to the position in the basin from  
184 about 50 m to more than 200 m. At the Nogaro 2 well, the thickness is close to 180 m. The  
185 lithostratigraphic cuts obtained in the Nogaro 2 well clearly identify the presence of the  
186 Lussagnet sands aquifer (between 920 and 1001 m deep), which, from a hydrogeological point  
187 of view, forms the upper part of the Eocene sand aquifer in that area. The Lussagnet sands  
188 aquifer overlies the Baliros sands aquifer, which is the productive zone of the reservoir (between  
189 1001 and 1092 m depth). This last part of the aquifer lies above a bioclastic calcareous layer  
190 (Horbaziou Formation) of low productivity (Infoterre, 2020a).

191 At Eauze, the Eocene aquifer is identified between 471 and 573 m. The upper part is  
192 constituted of clay interlayers and the real productive part of the reservoir (i.e. the exploited  
193 portion) lies between 504 and 573 m. It is made of sands and gravels of varying coarseness  
194 and overlies a grey calcareous horizon constituted of marls and sandstones with calcareous  
195 cement. At Dému, the well taps the Eocene aquifer between 740 and 780 m. The reservoir is  
196 overlaid by 12 m of sands and gravels and Nummulites sandstone seems to lie beneath, but  
197 the well was not drilled below this depth and the nature of the lower horizons is unknown.

198 The porosity of the quartz sand deposit is estimated at 20–35% (Housse and Maget, 1977;  
199 Douez et al., 2006). The average permeability (estimated from aquifer testing and modelling  
200 results) depends on the location and is generally accepted to range between  $1.5 \cdot 10^{-4}$  and  
201 approximately  $3 \cdot 10^{-5} \text{ m} \cdot \text{s}^{-1}$  (Labat, 1998; Seguin, 2003). The average interstitial velocity, using a  
202 gradient of 0.001 and an effective porosity of 20%, is close to  $5 \text{ m} \cdot \text{y}^{-1}$ . Groundwater flow is  
203 mainly oriented from SE towards NW but outflow from the aquifer is not fully known. The  
204 estimated apparent age of the groundwater (using  $^{14}\text{C}$  data and  $^{13}\text{C}$  data for corrections with the  
205 Pearson and Hanshaw model, 1970) is close to 25–35 ky (André et al., 2018), which is  
206 consistent with the effective advection calculated above.

207 The part of this aquifer that we studied is impacted hydraulically by gas storage at the  
208 Lussagnet and Izaute sites. With a maximum authorized capacity of 6.5 billion m<sup>3</sup>, the two  
209 storage facilities represent almost a quarter of France's underground storage capacity,  
210 supplying natural gas to the southwest of France and also feeding other French and European  
211 networks. The Lussagnet site has been implemented in 1957, prior to any piezometric  
212 measurements, and the Izaute site in 1981, which influence of the static water level is recorded  
213 since that date. Gas is stored on a relatively constant way throughout the year but monthly  
214 consumption in the winter can be almost five times as high as in the summer months (TEREGA,  
215 2020). Therefore, water pressure in the aquifer is submitted to high seasonal fluctuations (more  
216 than 10 bars), inducing groundwater level variations around the storage zone. Fluctuations are  
217 recorded all around the storage sites, like in Nogaro 2, Eauze and Dému, where static water  
218 level variations can reach several tens of meters for these three wells (Figure 3).

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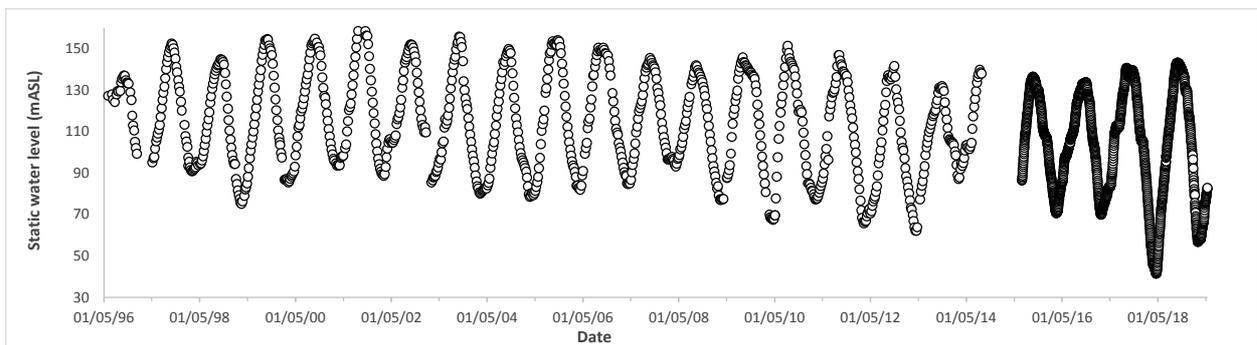
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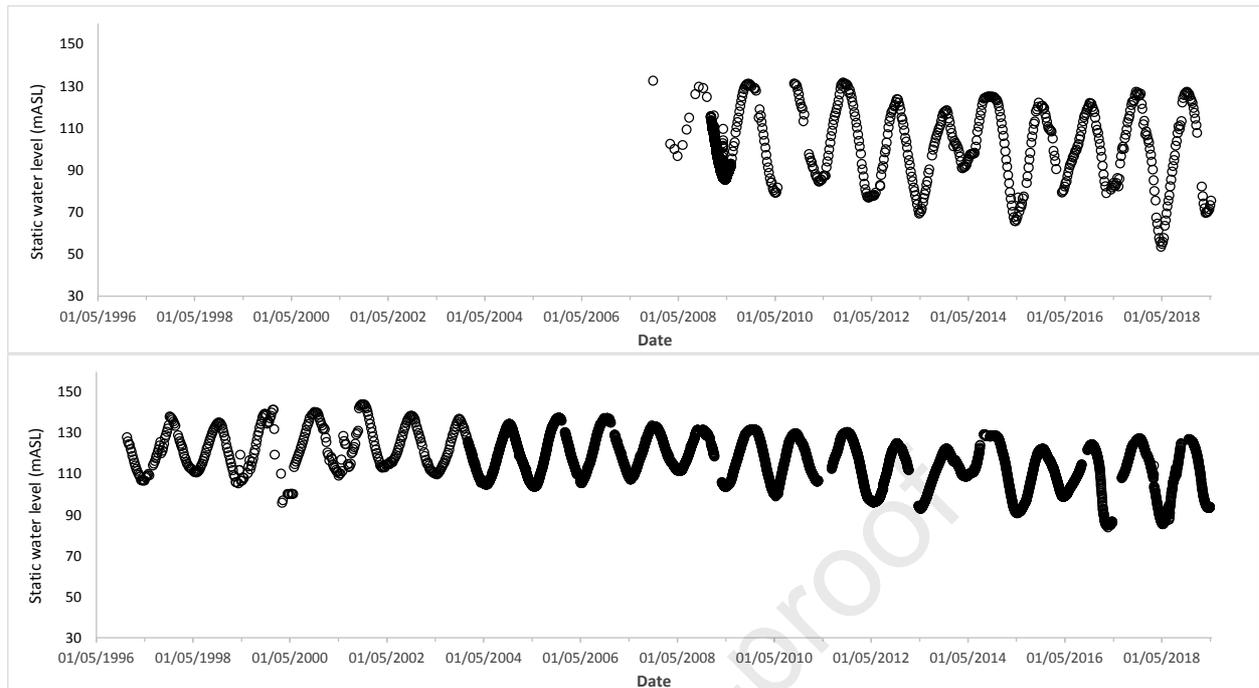
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231 **Figure 3 – Static water level recorded at three wells. Top: Nogaro 2; Middle: Eauze;**  
 232 **Bottom: Dému. The water level recording in Eauze starts in 2007, year of the wellbore**  
 233 **drilling.**

### 234 2.3 - Mineralogy

235 The mineralogy of the Eocene sands aquifer is relatively simple, containing mainly quartz  
 236 augmented with calcite, and, in some places, dolomite and K-feldspars (André, 2002). In the  
 237 Nogaro 2 well but also in other wells located in the zone of interest, pyrite indices were  
 238 recognized sometimes in the Lussagnet sands and sometimes under the base of the Lussagnet  
 239 sands aquifer, in the clay part of the Nummulites sandstones (Medium Eocene). More precise  
 240 attempts to characterize this pyrite were made during this study in order to determine the  $\delta^{34}\text{S}$   
 241 value of these sulfide minerals. Cuttings from a recently drilled well a few kilometres away from  
 242 Nogaro 2 were used to do this characterization. XRD analyses of these cuttings revealed the  
 243 presence of traces of pyrite (about 1% in mass). Extractions were then carried out in  
 244 laboratories. However, it has proved impossible to isolate the pyrite properly to carry out isotopic  
 245 analyses. The small amount, the grain size, and the pyrite being coated by quartz did not allow  
 246 further analysis.

247 The mineralogy of the molasse sediments, although less well investigated, is richer, with quartz,  
 248 feldspars, mica and several clay types (detrital limestone levels with sandy-clay deposits). At the  
 249 lower part of the molasse deposits, crystallised gypsum has been observed in cuttings at many  
 250 places.

251

### 252 **3 - Water chemistry**

253 This study is based on two types of data: complete measurements of water chemical  
254 composition recorded between 2016 and 2018 and historical data, corresponding to sulfate  
255 concentrations recorded for more than 20 years.

#### 256 **3.1 - Sampling and analytical methods**

257 Nine sampling campaigns (April, July, October 2016, January, March, June, October, December  
258 2017 and March 2018) and chemical analyses were carried out over two years. The  
259 investigated parameters measured on-site were physico-chemical data: temperature,  
260 conductivity (standardized to 25 °C), redox potential (Eh), pH. Parameters are measured at the  
261 wellhead, after purging the borehole. Water is collected only when physico-parameters are  
262 stable.

263 The water samples were collected in polyethylene bottles as raw samples for  $\delta^{18}\text{O}$ - $\delta^2\text{H}$ ,  $^{13}\text{C}$   
264 analyses and  $^{14}\text{C}$  activity measurements, and filtered through 0.45  $\mu\text{m}$  PVDF filters using a  
265 Nalgene filter apparatus for chemical and boron, sulfate and strontium isotopes analyses.  
266 Bottles dedicated to cation and strontium isotopes analysis were acidified with 15N ultrapure  
267  $\text{HNO}_3$  to  $\text{pH} < 2$ . A cadmium acetate solution was added to water samples dedicated to sulfate  
268 isotopes analysis to precipitate sulfides, decrease pH and eliminate potential bacteria. Samples  
269 were stored at 4 °C in the dark prior to analysis.

270 Major element concentrations are measured in BRGM's laboratory: Ca, Mg, Na, K and silica  
271 concentrations were measured by Inductively Coupled Plasma – Atomic Emission Spectroscopy  
272 (NF EN ISO 11885 of November 2009) and Cl,  $\text{SO}_4$  anions were analysed by ionic  
273 chromatography (Standard NF EN ISO 10304 of 1 July 2009). The accuracy for all element  
274 concentrations is 5 %, except Na and K with 10 %. Alkalimetry was measured by potentiometry  
275 and HCl titration according to Standard NF EN ISO 9963-1 February 1996, with an accuracy of  
276 15%.

277 Trace element concentrations (Al, B, Ba, Li, Mn, Sr, Br) were measured by inductively coupled  
278 plasma mass spectrometry according to Standard NF EN ISO 17294-2 of April 2005, with  
279 variable accuracy: Al 40%, B 15%, Ba 5%, Li 10%, Mn 10%, Sr 10% and Br 10%. Total iron  
280 ( $\text{Fe}_{\text{total}}$ ) concentration was measured by Inductively Coupled Plasma – Atomic Emission  
281 Spectroscopy (accuracy 10 %) and F by ionic chromatography with an accuracy of 5 %.

282 Accuracy and precision for major and trace elements was verified by repeated measurements of  
283 standard materials during the course of this study: namely Merck etalon (1  $\text{g.l}^{-1}$ ) for Ca, Mg, Na,

284 K, Fe, SiO<sub>2</sub>, Cl, F and a multi-element solution (10 mg.l<sup>-1</sup>) from Inorganic Ventures for trace  
285 elements.

286 Stable isotopes concentration ratios (<sup>2</sup>H/<sup>1</sup>H and <sup>18</sup>O/<sup>16</sup>O) of water molecules were analysed with  
287 a Finnigan<sup>®</sup> MAT 252 mass spectrometer connected to an automatic device, using the gas  
288 equilibration method (H<sub>2</sub> for hydrogen and CO<sub>2</sub> for oxygen). The isotopic ratios are expressed in  
289 ‰ vs V-SMOW (Vienna Standard Mean Ocean Water). Precisions are 0.8 ‰ for δD and 0.1  
290 ‰ for δ<sup>18</sup>O.

291 For <sup>34</sup>S<sub>SO4</sub> and <sup>18</sup>O<sub>SO4</sub> isotopic analysis, sulphides (precipitated as CdS after cadmium acetate  
292 adding) are first removed by filtration on 0.22 µm membrane. Then, dissolved sulfates are  
293 precipitated as BaSO<sub>4</sub> at pH < 4 by adding a BaCl<sub>2</sub> solution. The precipitate of BaSO<sub>4</sub> is then  
294 recovered on a 0.45 µm filter and dried at 50°C. For δ<sup>34</sup>S<sub>SO4</sub>, 250 µg of BaSO<sub>4</sub> are mixed with  
295 V<sub>2</sub>O<sub>5</sub> in a tin capsule, and injected in a flash combustion elemental analyzer (Flash EA) where  
296 BaSO<sub>4</sub> is reduced to SO<sub>2</sub> at 1700°C. The SO<sub>2</sub> gas, purified by gas chromatography is then  
297 analyzed by CF-IRMS (Continuous Flow Isotope Ratio Mass Spectrometer) on a Thermo  
298 Scientific Delta V Plus spectrometer. For δ<sup>18</sup>O<sub>SO4</sub>, 150 µg de BaSO<sub>4</sub> are placed in a silver  
299 capsule and injected into a graphite pyrolysis oven in a high temperature conversion elemental  
300 analyzer (TC/EA) at 1450°C. The CO gas resulting from the reaction between oxygen and  
301 graphite is purified, and analyzed by CF-IRMS on a Thermo Finnigan Delta Plus XP  
302 spectrometer. Calibration ranges (from -34.05 ‰ to +21.12 ‰ for δ<sup>34</sup>S<sub>SO4</sub>, and from -11.35 ‰ to  
303 +12.13 ‰ for δ<sup>18</sup>O<sub>SO4</sub>) are realised with three international standards (IAEA SO5, IAEA SO6,  
304 and NBS 127). The S and O isotope compositions are reported in the usual δ-scale in ‰ with  
305 reference to V-CDT (Vienna Canyon Diablo Troilite) and V-SMOW (Vienna Standard Mean  
306 Ocean Water). The sulfate-isotope compositions (δ<sup>34</sup>S<sub>SO4</sub> and δ<sup>18</sup>O<sub>SO4</sub>) were measured with a  
307 precision of ±0.3 ‰ vs. V-CDT for δ<sup>34</sup>S<sub>SO4</sub> and ±0.5 ‰ vs. V-SMOW for δ<sup>18</sup>O<sub>SO4</sub>.

308 Boron isotopic compositions were determined on a Finnigan<sup>®</sup> MAT262 solid source mass  
309 spectrometer in a dynamic mode. For these samples, water volumes corresponding to a boron  
310 quantity of 10 µg underwent a two-step chemical purification using Amberlite IRA-743 selective  
311 resin. The boron aliquot sample (2 µg) was then loaded onto a Ta single filament with graphite,  
312 mannitol and Cs, and the B isotopes were determined by measuring the Cs<sub>2</sub>BO<sub>2</sub><sup>+</sup> ion. Total  
313 boron blank is less than 10 ng. Purified samples are always analysed twice. The values are  
314 given using the δ-notation (expressed in ‰) relative to the NBS951 boric acid standard. The  
315 <sup>11</sup>B/<sup>10</sup>B of replicate analysis of the NBS951 boric acid standard after oxygen correction was  
316 4.05387 ± 0.00120 (2σ, n = 192) during this period (April-2016 to May-2018). The reproducibility  
317 of the δ<sup>11</sup>B determination is then ± 0.3‰ (2σ). The internal uncertainty is often better than 0.2‰

318 ( $2\sigma_m$ ). Long-term accuracy and reproducibility of the overall procedure were verified by the  
319 repeated measurements of the IAEA-B1 seawater standard (Gonfiantini et al. 2003) for which  
320 the mean  $\delta^{11}\text{B}$  value obtained is  $39.20\text{‰} \pm 0.30$  ( $2\sigma$ ,  $n=93$ ) in accordance with the accepted  
321 value for seawater.

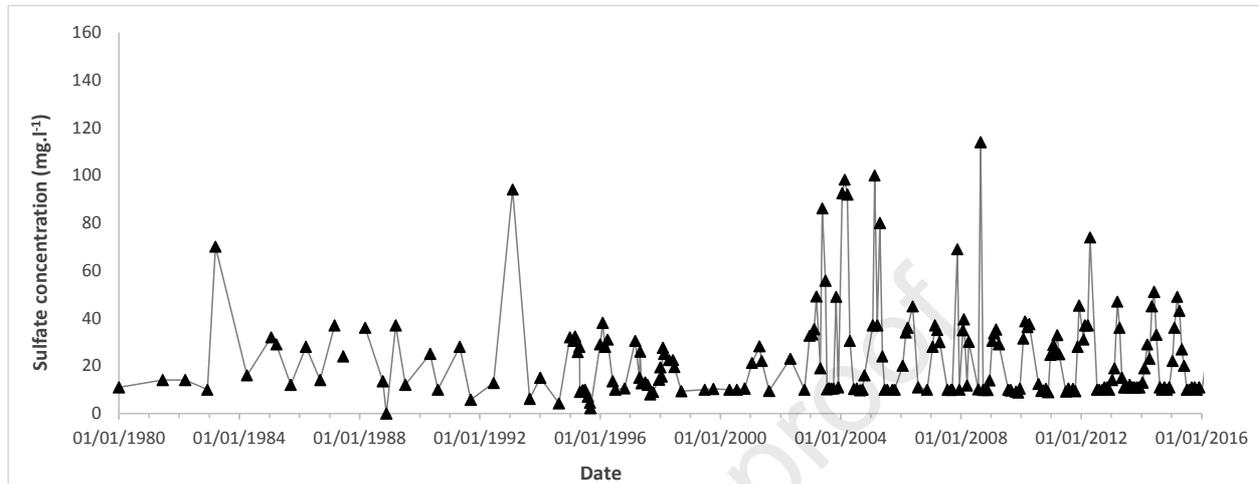
322 Chemical purification of Sr was performed with an ion-exchange column (Sr-Spec) before mass  
323 analysis according to a method adapted from Pin and Bassin (1992), with total blank  $<0.5$  ng for  
324 the entire chemical procedure. After chemical separation, around 150 ng of Sr was loaded onto  
325 a tungsten filament with tantalum activator and analyzed with a Finnigan<sup>®</sup> MAT262 multi-  
326 collector mass spectrometer. The  $^{87}\text{Sr}/^{86}\text{Sr}$  ratios were normalized to a  $^{86}\text{Sr}/^{88}\text{Sr}$  ratio of 0.1194.  
327 An average internal precision of  $\pm 10$  ppm ( $2\sigma_m$ ) was obtained and reproducibility of the  $^{87}\text{Sr}/^{86}\text{Sr}$   
328 ratio measurements was tested through repeated analyses of the NBS987 standard for which  
329 we obtained, during the overall duration of this study, a mean value of  $0.710246 \pm 0.000011$   
330 ( $2\sigma$ ,  $n = 294$ ). Sample ratios were normalized to the certified value of the NBS987 (0.710240).

331 Carbon stable isotopes ( $^{13}\text{C}/^{12}\text{C}$ ) and  $^{14}\text{C}$  activity were analysed by Beta Analytic Inc. Water was  
332 first acidified with orthophosphoric acid under vacuum to get  $\text{CO}_2$ . The gas is purified and a  
333 small aliquot fraction was used for the measurement of  $^{13}\text{C}/^{12}\text{C}$  ratio by Isotopic Ratio Mass  
334 Spectrometry (IRMS). Measured  $^{13}\text{C}/^{12}\text{C}$  ratios are calculated relative to the PDB-1 standard.  
335  $\text{CO}_2$  was reduced by  $\text{H}_2$  into graphite over a cobalt catalyst. The  $^{14}\text{C}$  measurements were  
336 performed by Accelerator Mass Spectrometry (AMS). The analytical result (in pMC) is obtained  
337 by measuring sample  $^{14}\text{C}/^{13}\text{C}$  relative to the  $^{14}\text{C}/^{13}\text{C}$  in Oxalic Acid II (NIST-4990C). The typical  
338 analytical uncertainty is about 0.1 pMC ( $1\sigma$ ).

### 339 **3.2 - Historical data**

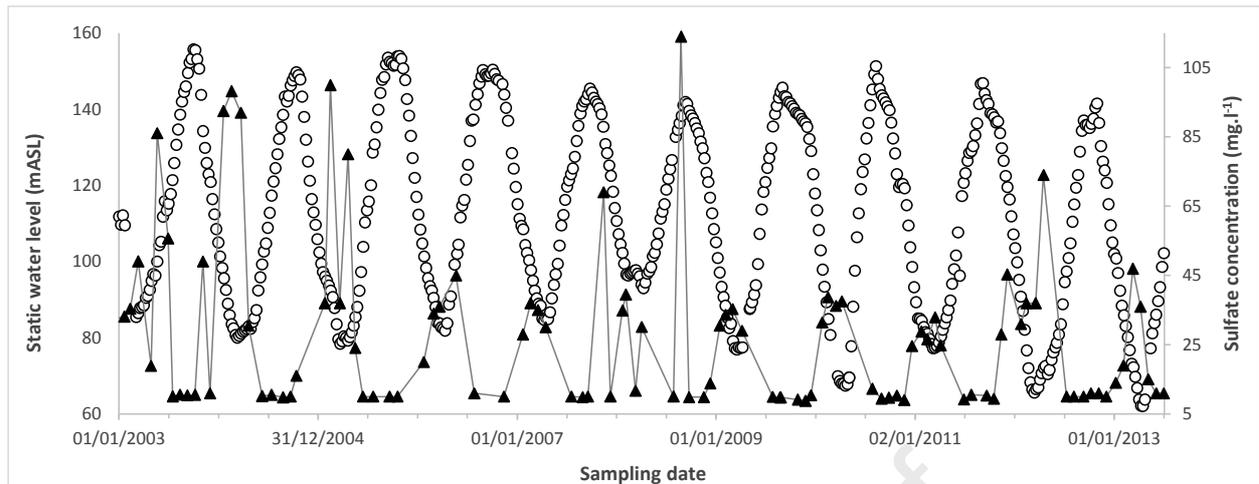
340 Nogaro 2 is a well used to provide drinking water. Because of this use, the water quality is  
341 regularly controlled. Since the sulfate concentration of waters exceeds sometimes drinking  
342 waters regulations (in France, the breakthrough value of sulfate concentration is  $250 \text{ mg.l}^{-1}$ ), a  
343 monthly monitoring is organized by the Regional Health Agency and monitoring is managed by  
344 the laboratory of the Gers department. However, this monitoring only focus on electrical  
345 conductivity and sulfate concentrations measurements without any information on other major  
346 and trace elements. All the chemical data acquired by both laboratories are registered on ADES  
347 website (ADES, 2020), a national database available for consultation. This hydrogeochemical  
348 monitoring revealed the variable sulfate concentration over time (Figure 4). From 2003-2015,  
349 between 6 and 12 measurements were made per year. While the chemical composition of the  
350 waters of the Eocene Sands aquifer varies only moderately over time, the waters show  
351 seasonal variation in sulfate concentrations. The lowest concentrations were of the order of 10

352  $\text{mg.l}^{-1}$ , while the strongest reached values greater than  $100 \text{ mg.l}^{-1}$ . Although sulfate was  
 353 monitored regularly, available water analyses were often incomplete and it was difficult to  
 354 correlate these variations in sulfate content with variations in other chemical elements.



355  
 356 **Figure 4 – Sulfate concentrations for waters in the Nogaro 2 well between 1980 and 2016**

357  
 358 A visual comparison of piezometric levels and measured concentrations shows that high sulfate  
 359 concentrations are found when piezometric levels are low (Figure 5). There is therefore an  
 360 apparent anti-correlation between water level measurements and sulfate concentration  
 361 measurements. We therefore assume the preeminent role of the pressure variations in the  
 362 aquifer. We also observe that the shape of concentration cycles are different from the shape of  
 363 hydraulic head variations: “concentration plateaus” of variable length separate the sulfate peaks  
 364 whereas the hydraulic head looks like a sinusoidal curve. So the sulfate plateau reveals a  
 365 minimum concentration of this element ( $10 \text{ mg.l}^{-1}$ ) in the aquifer. This  $10 \text{ mg.l}^{-1}$  value does not  
 366 correspond to analytical limitations but to a real value of sulfate concentration in the reservoir.



367  
 368 **Figure 5 – Water levels (open black circle) and sulfate concentrations (black triangles**  
 369 **with grey line) for water from the Nogaro 2 well between 2003 and 2013**

370  
 371 The Eauze well has been drilled quite recently (in 2007) and there has not been regular  
 372 monitoring of sulfate concentration for this well (only 4 data points are available over the period  
 373 2007-2016). However, given the piezometric amplitudes over this period and the geographical  
 374 proximity to the Nogaro 2 well, the question arises of how dissolved sulfate behaves in the  
 375 water from this well.

376 The Dému well also has high piezometric amplitudes (about 30 m - Figure 3). However, based  
 377 on the available data before this study, no correlation between piezometric level and  
 378 concentrations could be found.

379 Consequently, the chemical cyclic behaviour observed at the Nogaro 2 well and potentially in  
 380 other wells of the sector raises many questions on the origin of these fluctuations. However,  
 381 given the available data and particularly the small number of complete chemical analyses, we  
 382 decided to carry out quarterly monitoring of the chemical composition of the waters of the three  
 383 wells. The aim was to be able to understand the reason for these variations, both in terms of  
 384 chemistry and as an inferred consequence of the system's hydrodynamic behaviour.

### 385 3.3 - Results

#### 386 3.3.1 - Physico-chemical parameters

387 Wellhead measured temperatures – reaching up to 53.9°C at Dému – show some variations for  
 388 the three wells (see Appendix – Table A-1). These temperature differences are mainly due to  
 389 pumping rates and cooling conditions within the hundreds of meters of casings: the wells are

390 not pumped continuously since the three of them are used for drinking water, with pumping  
391 fluctuations according to the hour of the day. The water temperatures of each well are  
392 consistent with the mean annual air temperature (MeteoFrance, 2020) and the mean  
393 geothermal gradient (ranging between 2.8 and 3.2°C/100 m) observed in the Aquitaine Basin  
394 (Housse and Maget, 1977).

395 Electric conductivity does not vary at Eauze whereas variations were observed of up to 10 % at  
396 Dému and 30 % at Nogaro 2 (See Appendix - Table A-1). These variations were due to  
397 changes in major element concentrations as described below.

398 Redox potential fluctuated greatly for the three wells, ranging from -300 to +150 mV. The values  
399 were mostly negative, which is coherent with reduced waters pumped at such depths. However,  
400 interpreting such fluctuations is tricky since this parameter is always difficult to measure,  
401 especially for moderately hot waters containing oxidized and reduced species (e.g. H<sub>2</sub>S, sulfate,  
402 iron). The redox potential often corresponds to a global value impacted by different redox  
403 couples. We did not use this parameter for the interpretations.

404 Concerning pH, the values ranged between 7.1 and 7.8, which is coherent with waters whose  
405 pH is mainly controlled by calco-carbonic equilibrium with a relative low CO<sub>2</sub> partial pressure,  
406 around 10<sup>-2</sup> atm (André et al., 2005).

### 407 **3.3.2 - Major elements**

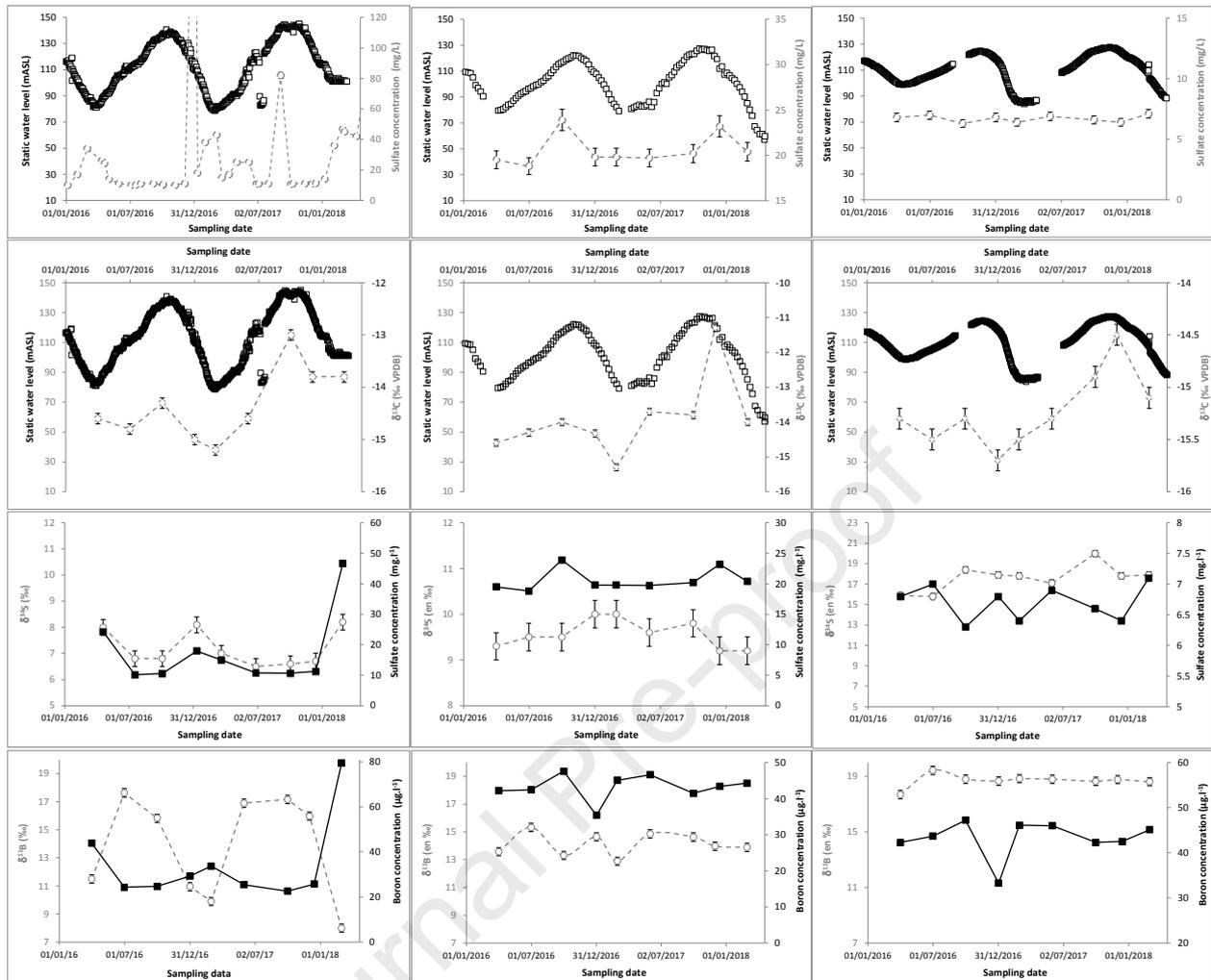
408 The major element concentrations are given in Appendix – Table A-2. Waters show a calcium  
409 bicarbonate facies, like most of the waters from the Eocene aquifer (André et al., 2005). They  
410 have a total dissolved solid concentration lower than 1000 mg.l<sup>-1</sup>. Waters are generally at the  
411 equilibrium with quartz, calcite and a CO<sub>2</sub> partial pressure close to 10<sup>-2</sup> atm, whereas they are  
412 undersaturated with respect to sulfate minerals (see calculated saturation indices in Appendix –  
413 Table A-7). Since most of them have constant concentrations with time, Figure 6 focuses on  
414 sulfate alone. It shows how sulfate concentrations changed between January 2016 and March  
415 2018 for the three investigated wells. For Nogaro 2, in addition to the nine sampling campaigns  
416 done by BRGM, the monthly sulfate concentration measurements organized by the Regional  
417 Health Agency are plotted on Figure 6. For Nogaro 2, three major sulfate concentration peaks  
418 were measured from January to April 2016 (with a maximum value of 34 mg.l<sup>-1</sup>), from March to  
419 June 2017 (maximum value of 43 mg.l<sup>-1</sup>) and from March to May 2018 (maximum value of  
420 72 mg.l<sup>-1</sup>). Sulfate concentrations for these peaks were 1.5 to 5 times the “reference sulfate  
421 concentration”, estimated at 10 mg.l<sup>-1</sup>. Two very high sulfate concentrations were recorded  
422 during this period, the first one 3 January 2017 (with a value close to 300 mg SO<sub>4</sub>.l<sup>-1</sup>) and the

423 other 5 September 2017 (with a value of about 82 mg SO<sub>4</sub>.l<sup>-1</sup>). For the first one, the major  
424 increase of sulfate concentration is consistent with the water conductivity measurements,  
425 reflecting a substantial increase of water mineralization. However, as the major elements  
426 concentrations are not available for this sampling, it is impossible to confirm whether the value  
427 is consistent with the groundwater sulfate concentrations (analytical error, filtration issues in the  
428 samples, sulfate enriched particles, etc.) and with which other elements the sulfate would be  
429 correlated. It is also important to underline the brevity of this event since the sulfate  
430 concentration is about 18 mg.l<sup>-1</sup> one week later.

431  
432 The increased sulfate concentration in the Nogaro 2 waters seems to be correlated with  
433 increased calcium and magnesium concentrations (See Appendix - Table A-2). The (Ca+Mg)/Cl  
434 ratio clearly shows brief enrichment in Ca and Mg and the (Ca+Mg)/SO<sub>4</sub> ratio decreases  
435 drastically, underlying the enrichment in both calcium and sulfate in the solution. The Dému well  
436 waters are the most stable, with no observable seasonal variations in major anion and cation  
437 concentrations. Each calculated ratio confirms that these concentrations remain stable over time  
438 (Figure 7). At the Eauze well, some variations in sulfate concentrations were observed in  
439 October 2016 and December 2017. The increase was a much smaller proportion than at  
440 Nogaro 2. The enrichment factor was about 1.2 compared to a base concentration of about 19-  
441 20 mg.l<sup>-1</sup>. The ratio (Ca+Mg)/SO<sub>4</sub> was weakly impacted by this increased sulfate concentration  
442 even though a slight decrease was observed in October 2016 and December 2017.

443 The piezometric level of the Nogaro 2 well (Figure 6) was anticorrelated with the increases in  
444 sulfate concentrations in late winter-early spring 2016, 2017 and 2018: during these periods, the  
445 sulfate concentration was at its highest when the piezometric level was at its lowest. These  
446 observations hold if we exclude the two inexplicable peaks measured in January 2017 and  
447 September 2017. For these two peaks, there are no anomalies on the piezometric data that  
448 could explain these change in concentrations.

449 While at Nogaro 2, peaks in sulfate concentration were anti-correlated with the piezometric  
450 level, for Eauze there is an almost positive correlation between sulfate concentration and  
451 piezometric variations. Much more regular sampling over time (as in Nogaro 2) would help to  
452 better define peak periods and thus better understand the links between these two variables  
453 (phase shift, lag or simultaneous signal relative to the other).



454  
 455 **Figure 6 – Comparison between data measured during the project for wells: Nogaro 2**  
 456 **(left column), Eauze (centre column) and Dému (right column). First line of graphics: total**  
 457 **sulfate concentration (dashed line) and static water level (black open symbols); second**  
 458 **line of graphics:  $\delta^{13}\text{C}$  content (dashed line) and static water level (black symbols); third**  
 459 **line of graphics:  $\delta^{34}\text{S}$  in sulfates (dashed line) and total sulfate concentration (full line);**  
 460 **fourth line of graphics:  $\delta^{11}\text{B}$  (dashed line) and total dissolved boron concentration (full**  
 461 **black line).**

### 462 3.3.3 - Trace elements

463 Variations in Al, B, Ba, F, Fe, Li, Mn, Sr and Br concentrations were measured in the waters of  
 464 the three wells for all sampling campaigns (See Appendix - Table A-3).

465 Except the decrease in the strontium content in December 2017, for which we see no particular  
 466 explanation (Perhaps a sampling or analytical problem?), strontium and barium concentrations  
 467 were stable over time for the three wells (See Appendix - Table A-3). This stability in strontium  
 468 is confirmed by isotope  $^{87}\text{Sr}$  (see paragraph below). Barium concentration was low in waters

469 and does not seem to be controlled by barite (see Appendix – Table A-7). The saturation  
470 indices of barite calculated with PHREEQC code (Parkhurst and Appelo, 2013) were close to -  
471 0.8/-0.9 for Demu waters and to -0.20/-0.30 for Eauze waters. For Nogaro, because of the  
472 variation in sulfate concentration, the saturation indices range between 0.02 during sulfate  
473 peaks (like in March 2018) to -0.6 during low sulfate concentration phases (like in June 2017). Li  
474 concentrations do not vary with time, with values ranging between 8 and 15  $\mu\text{g.l}^{-1}$ . Al  
475 concentrations do not exceed 2  $\mu\text{g.l}^{-1}$  and it seems controlled in some cases by equilibrium with  
476 montmorillonite or illite (See Appendix - Tables A-3 and A-7).

477 Finally, boron is the trace element that undergoes variations for all three wells. For the Nogaro 2  
478 well, this variation is cyclical, with higher concentrations in April 2016, March 2017 and March  
479 2018 (Figure 6). The concentration reaches as much as 80  $\mu\text{g.l}^{-1}$  and falls as low as close to  
480 20  $\mu\text{g.l}^{-1}$ . The variation of the concentration profile over time is similar to that of sulfate, with an  
481 increase in April 2016, March 2017 and March 2018, and somewhat of a plateau for the other  
482 measurements (around 20  $\mu\text{g.l}^{-1}$ ). For Eauze and Demu, fluctuations were observed but in a  
483 less extent than in Nogaro since the concentration varies generally between 42 and 48  $\mu\text{g.l}^{-1}$ .  
484 There is no evidence of a cyclic evolution of the boron concentration. One value measured in  
485 January 2017 for both wells seems to fall outside of the range. It is lower by about 20 % than all  
486 the other measurements at these two wells but there is no coincidence with abnormal values of  
487 boron isotopes (See paragraph on  $^{11}\text{B}$  isotope and Figure 6).

### 488 3.3.4 - Isotopes

489 Like for major and trace elements, we screened a wide range of stable and radioactive isotopes  
490 to identify potential tracers of the chemical mechanisms responsible for the observed variations.  
491 Isotopes of water ( $^2\text{H}$  and  $\delta^{18}\text{O}$ ) and strontium isotopes ( $^{87}\text{Sr}$ ) were measured during the first  
492 sampling campaigns (April 2016 to January 2017). They both had largely constant values and  
493 an absence of cyclic variations (see Appendix – Tables A-4 and A-5). Therefore, we focused  
494 more on interpreting the carbon, sulfate and boron isotopes. Isotopic compositions for stable  
495 isotopes of  $^{34}\text{S}$ ,  $^{11}\text{B}$  and  $^{13}\text{C}$  are reported in the usual  $\delta$ -scale, with  
496  $\delta_{\text{sample}} (\text{‰}) = \{(R_{\text{sample}} / R_{\text{reference}}) - 1\} \times 1000$ , where R is the ratio of the numbers of heavy and  
497 light isotopes.

#### 498 • $^{13}\text{C}$ and $^{14}\text{C}$ in carbonates

499 Carbon-13 and carbon-14 in carbonates were analysed during the study of the three wells (See  
500 Appendix - Table A-6).

501 The waters of the Nogaro 2 show relatively stable carbon-14 activities, with small amplitude  
502 variations around 2 pMC (see also Andre et al., 2019). The apparent age of the waters is about  
503 -30,000 years BP according to Pearson and Hanshaw model (1970).  $\delta^{13}\text{C}$  has cyclic variations,  
504 which seem to be correlated with the piezometric level over the period 2016-2018, with a high  
505 value for this parameter at the maximum piezometric level in September 2017 (Figure 6).

506 We also observed the same variations and correlation between  $\delta^{13}\text{C}$  and the piezometric level  
507 for the two other wells.  $\delta^{13}\text{C}$  variations reached about 3 ‰, as in Eauze, or only 1 ‰, as in  
508 Nogaro 2 and Dému. These variations could indicate that potential chemical reactions and/or  
509 water mixing processes could affect the  $\delta^{13}\text{C}$  value in solution.

#### 510 • $^{34}\text{S}$ in sulfates

511 For the Nogaro 2 well, variations in sulfur-34 follow the variations in total sulfur (Figure 6).  
512 Indeed, when the sulfate concentration is close to  $10 \text{ mg.l}^{-1}$ , the  $\delta^{34}\text{S}$  value is close to +7.0 ‰.  
513 Though total sulfate concentration and sulfur-34 increase, variations in sulfur-34 are relatively  
514 small, as they do not exceed 2 ‰, even when the sulfate content is multiplied by 4, as in March  
515 2018.

516 To sum up for the Nogaro 2 well, when the piezometric level is high, the sulfate content  
517 decreases and carbon-13 content tends to increase (anti-correlation between sulfate and  
518 carbon-13).

519 For the Eauze well, the relationship between the sulfate concentration and the  $\delta^{34}\text{S}$  value is  
520 much less pronounced than at Nogaro 2. The small seasonal variations in sulfate  
521 concentrations (lower than  $5 \text{ mg.l}^{-1}$ ) correlated with piezometric fluctuations and the small  
522 amplitudes recorded for  $\delta^{34}\text{S}$  do not allow us to infer an accurate correlation.

523 For the Dému well, the variations in total sulfur concentration are very low (less than  $1 \text{ mg.l}^{-1}$ )  
524 and confirmed by the absence of  $\delta^{34}\text{S}$  variations. We note that the  $\delta^{34}\text{S}$  was quite high (about  
525 +17 ‰), much higher than at the Eauze well (about +9.5 ‰), which seems to indicate a different  
526 origin for sulfur in solution.

#### 527 • $^{11}\text{B}$

528 The waters of the Nogaro 2 well show a cyclic and seasonal variation for  $\delta^{11}\text{B}$  value. When the  
529 boron content increased in water (April 2016, March 2017 and March 2018), the  $\delta^{11}\text{B}$   
530 significantly decreased to reach the order of +10 ‰ (Figure 6). When boron levels were lower  
531 (on the order of  $25 \text{ mg.l}^{-1}$ ),  $\delta^{11}\text{B}$  increased to +18 ‰. This finding seems to indicate a mix of the  
532 initial water with a  $^{11}\text{B}$ -depleted solution. For Eauze well, the variations of  $\delta^{11}\text{B}$  values are limited

533 to 2 ‰. The relation between  $\delta^{11}\text{B}$  and the total boron concentration is less remarkable than for  
534 Nogaro 2 even if a cyclic variation can be supposed between mid 2016 and mid-2017. For  
535 Demu well,  $\delta^{11}\text{B}$  values are stable with time.

### 536 3.4 – Geochemical modelling

537 Analyses of major elements, trace elements and isotopes in the Nogaro 2 well waters confirm  
538 cyclic variations in sulfate concentrations already observed in the chemical time series. These  
539 sulfate concentration increases are correlated with increases in boron levels and anti-correlated  
540 with static water level and  $^{13}\text{C}$  content in the waters.

541 Based on sulfur-34 isotopic data, sulfate enrichment seems to come from a source with a  $\delta^{34}\text{S}$   
542 greater than the base value in the reservoir (estimated here at +6.5 ‰ CDT). For boron, the  
543 increase in its total concentration coincides with a decrease of  $\delta^{11}\text{B}$ . In this case, the source of  
544 boron responsible for the increase in concentration has a lower  $\delta^{11}\text{B}$  value than the base value  
545 in the reservoir (estimated at +17.5 ‰).

546 To interpret these field results, simulations with the PHREEQC software (Parkhurst and Appelo,  
547 2013) were carried out with the *iso.dat* database released with the code. Since boron-11 is not  
548 in the database, the new species was implemented: parameters used to calculate the specific  
549 volume of  $\text{H}_3\text{BO}_3$  are from SUPCRT92 (Johnson et al., 1992), whereas the standard value  
550 (4.04362 ‰) for  $^{11}\text{B}/^{10}\text{B}$  is from Catanzaro et al. (1970). This software is particularly used in  
551 geosciences because of its adaptability to geochemical problems of varying complexity. It offers,  
552 among other things, the possibility of making geochemical calculations on isotopes, taking into  
553 account the ratios of different species. The simulations consisted of reproducing variations in  
554 sulfate and boron levels in the Nogaro 2 waters since this well presents the most significant  
555 variations. The main objective was to be able to establish more precisely the values of  $\delta^{34}\text{S}$  (in  
556 sulfate) and  $\delta^{11}\text{B}$  (for boron) that participate in these cyclical concentration variations. All  
557 modelling was done in a batch system in which water mixtures (in the form of additions) were  
558 simulated (Figure 7).

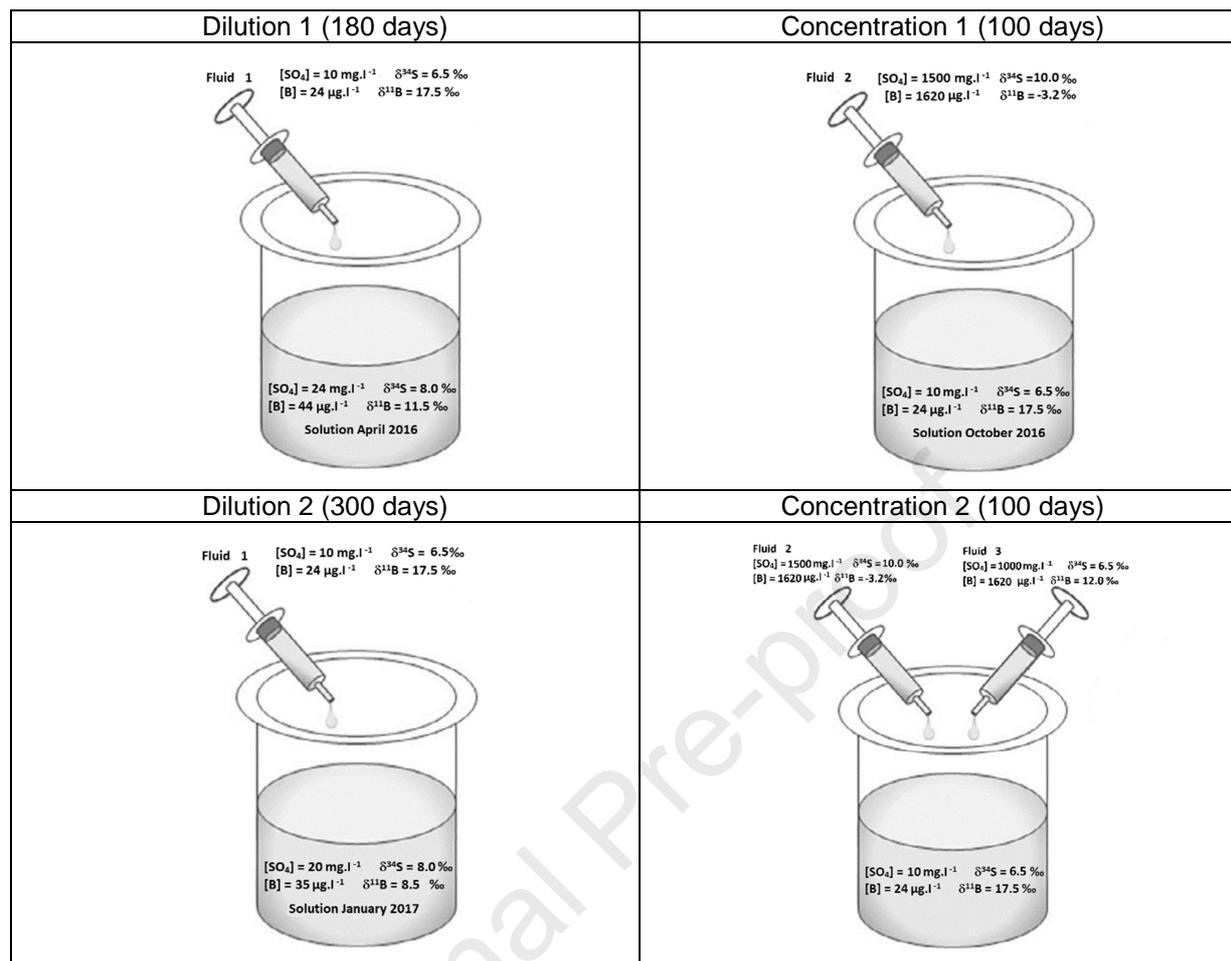
559 As shown in Figure 8, the initial water used for the simulations corresponded to the Nogaro 2  
560 water analysed in April 2016, the beginning of quarterly samples, with an initial sulfate  
561 concentration of around  $24 \text{ mg.l}^{-1}$  (and  $\delta^{34}\text{S} = +8.0 \text{ ‰}$ ) and a boron content of  $44 \text{ } \mu\text{g.l}^{-1}$  (and  
562  $\delta^{11}\text{B} = +11.5 \text{ ‰}$ ). The numerical simulations consisted of modelling two cycles, each comprising  
563 two stages, namely a dilution phase (by mixing with a sulfate- and boron-depleted fluid) and a  
564 concentration phase (by mixing with a fluid enriched with sulfate and boron). The durations of

565 the dilution and concentration phases are consistent between simulations and on-site  
566 measurements.

567 A first dilution phase lasting 180 days was then simulated. The dilutions were done by  
568 successive additions of a Fluid 1 whose sulfate and boron contents were respectively  $10 \text{ mg.l}^{-1}$   
569 and

570  $24 \text{ }\mu\text{g.l}^{-1}$  (Figure 7). If Fluid 1 was assumed to be initially in equilibrium with calcite and to have a  
571  $\text{CO}_2$  partial pressure of  $10^{-2} \text{ atm}$ , this equilibrium is not imposed during all the dilution phase (no  
572 constraints on the calco-carbonic equilibrium). Initial pH of water is close to 7.35 and  $\text{Eh} = 0 \text{ mV}$   
573 (consistent with measured values – see Appendix – Table A-1). The mixing consisted in adding  
574 Fluid 1 by 5 % in volume every day. The resulting sulfate and boron concentrations fell to  $10$   
575  $\text{mg.l}^{-1}$  for sulfate (and  $\delta^{34}\text{S} = +6.5 \text{ ‰}$ ) and  $24 \text{ }\mu\text{g.l}^{-1}$  for boron (and  $\delta^{11}\text{B} = 17.5 \text{ ‰}$ ). These  
576 modelled variations were consistent with the measured groundwater concentrations, simulating  
577 both the decrease and the plateau of sulfate concentration (Figure 8).

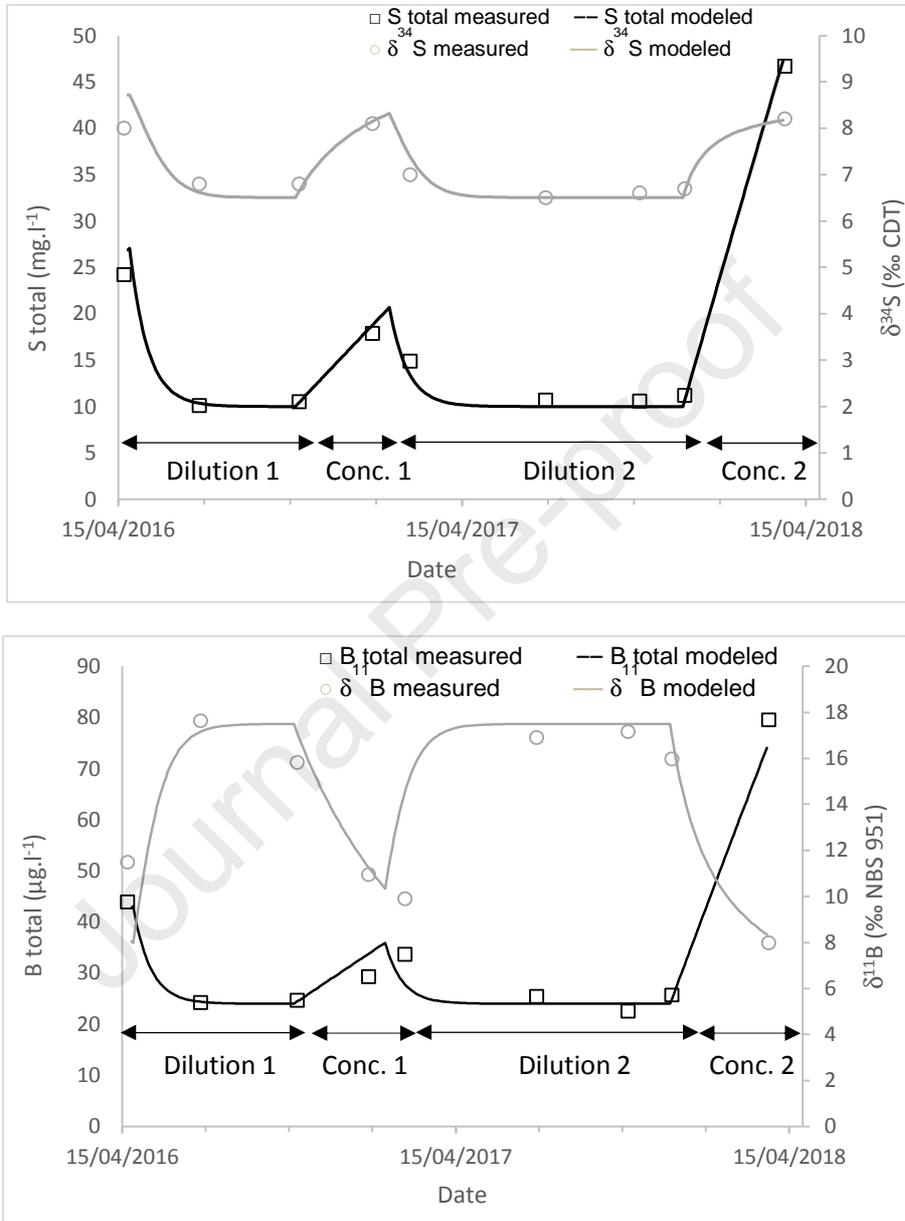
578



579 **Figure 7 – Conceptual model of the geochemical modelling of the dilution and**  
 580 **concentration stages impacting the Nogaro 2 waters.**

581 Next, a first concentration phase was simulated over a period of 100 days (Figure 7). This  
 582 phase was shorter since it only represented the increased sulfate concentration whereas the  
 583 previous included both the decreasing sulfate concentration and the plateau. The added  
 584 solution (called Fluid 2) had sulfate and boron concentrations of 1500 mg.l<sup>-1</sup> and 1620 µg.l<sup>-1</sup>,  
 585 respectively. Fluid 2 was assumed to be in equilibrium with calcite to impose the carbon content  
 586 corresponding to a CO<sub>2</sub> partial pressure around 10<sup>-2.1</sup> atm. The isotope values were +10.0 ‰  
 587 and -3.2 ‰ for sulfur of sulfate and boron, respectively. These concentration and isotope values  
 588 were calibrated to best represent the measured data. Among all the potential solutions, we took  
 589 chose to consider the mixing fluid in equilibrium with gypsum, at the temperature of the  
 590 reservoir. Since this water-mineral equilibrium fixes the sulfate concentration, it was then  
 591 possible to determine both the amount of the added fluid and the δ<sup>34</sup>S value of sulfate to match  
 592 the measured data. The boron concentration was characterized according to the amount of fluid  
 593 added and finally, the boron isotope value was defined. Fluid 2 was added in 0.0075 % volume  
 594 increments every day, which is a far lower percentage than during dilution 1. That discrepancy

595 between mixing proportions is addressed in section 4. The consequence of these successive  
 596 additions was an increase in sulfate and boron concentrations and  $\delta^{34}\text{S}$  and a decrease in  $\delta^{11}\text{B}$   
 597 over time (Figure 8). The maximum peak values are respected.



598

599

600 **Figure 8 – Variations with time of (a) total sulfate concentration and  $\delta^{34}\text{S}$ ; (b) total boron**  
 601 **concentration and  $\delta^{11}\text{B}$  in the Nogaro 2 water. Dilutions and concentration correspond to**  
 602 **the stages defined in Figure 7. Symbols are data measured during this study.**

603 The second cycle began with a dilution phase, significantly longer than the dilution during phase  
 604 1 (300 days), so we reached the base values in the aquifer. Then a second concentration phase  
 605 over 100 days followed. During this phase, the maximum boron and sulfate concentrations were  
 606 much higher than in the first concentration phase, whereas the final values of the isotopic

607 values were similar to the initial values. This suggests that the mix is more complex than in the  
608 first case and another source of sulfate and boron is required. A new “recharge” solution (called  
609 Fluid 3) had to be defined, with sulfate concentrations on the order of  $1000 \text{ mg.l}^{-1}$  and a boron  
610 concentration of about  $1620 \text{ }\mu\text{g.l}^{-1}$ . Fluid 3 was assumed to be in equilibrium with calcite to  
611 impose the carbon content corresponding to a  $\text{CO}_2$  partial pressure around  $10^{-2.1}$  atm. Isotope  
612 values for boron and sulfur of sulfate were  $+12 \text{ ‰}$  and  $+6.5 \text{ ‰}$  CDT, respectively. As previously,  
613 these values were numerically determined to best represent the measured data. Each Fluid, 2  
614 and 3, was added in increments of  $0.015 \text{ ‰}$  by volume every day. These additions increased  
615 the sulfate and boron contents in the mixture (to reach respectively  $46 \text{ mg.l}^{-1}$  and  $80 \text{ }\mu\text{g.l}^{-1}$ ),  
616 while respecting the values of measured isotopic ratios.

617 These geochemical simulations allowed us to estimate the concentrations and isotope  
618 compositions of waters that can mix with the Eocene aquifer groundwater to explain the cyclical  
619 variations, especially in sulfate and boron. These simulations relate to “classic” variations in  
620 sulfate concentration, but they do not represent exceptional variations, such as the sulfate  
621 concentration of  $300 \text{ mg.l}^{-1}$  recorded in January 2017 as part of the Health monitoring of  
622 Nogaro 2 waters. According to these simulations, the “recharge” water used during the  
623 concentration phases had significantly higher sulfate and boron content than the waters of the  
624 aquifer.

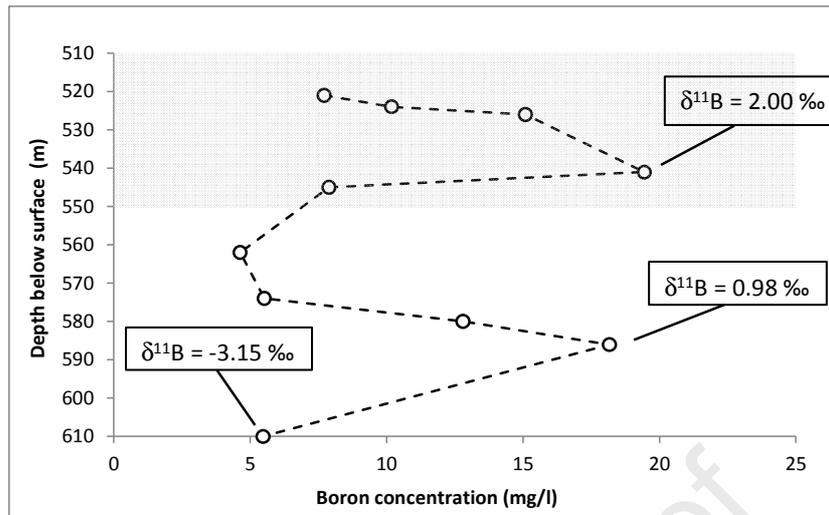
#### 625 **4 – Discussion**

626 This study confirms the cyclic variations of sulfur concentration observed during recent years in  
627 the waters of Nogaro 2 well and also, but with a lower amplitude, at Eauze. There are no  
628 variations in Dému, which is farther from Nogaro 2. As discussed in André et al. (2002), sulfur in  
629 solution can have different origins. Some can come from precipitation (since water has meteoric  
630 origins), from gypsum dissolution, or from the oxidation of reduced sulfur minerals like pyrite.  
631 Our study does not describe explicitly the potential chemical mechanism responsible for these  
632 variations. But the numerical approach used in this study allows us to introduce some  
633 hypotheses to explain these cyclic variations.

634 First, it seems that the Eocene groundwater (named Fluid 1) close to the Nogaro 2 well has a  
635 “base” sulfate concentration value of  $10 \text{ mg.l}^{-1}$  and a  $\delta^{34}\text{S}$  of  $+6.5 \text{ ‰}$  CDT, which could reflect  
636 various origins for sulfur (mainly gypsum dissolution and a small part from pyrite oxidation  
637 according to André et al., 2002). The cyclic concentration increases could be due to mixing with  
638 a sulfate-enriched fluid. Many numerical solutions are possible since the chemical compositions  
639 of the added fluids and the proportion of the mix are unknown. We selected the option to  
640 consider the mixing fluid in equilibrium with gypsum at the temperature of the reservoir for two

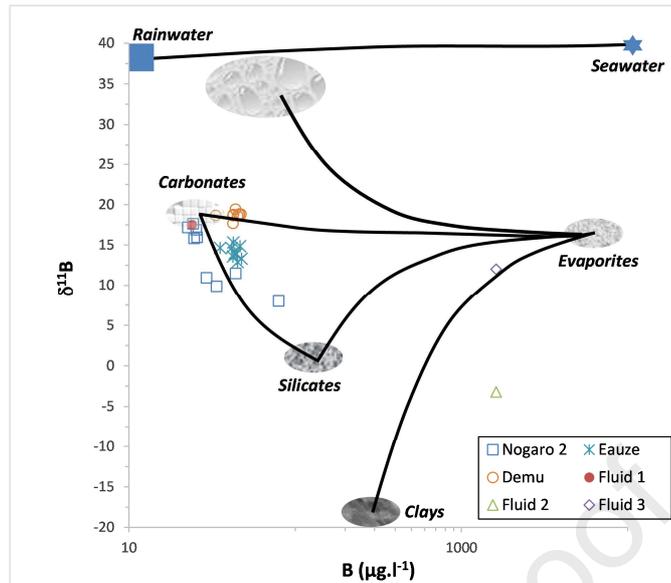
641 reasons: first gypsum has been identified in the molasse horizon, at the top of the aquifer.  
642 Molasse sediments are known to be a low-permeable media, fully saturated with water.  
643 Because of the long contact time between water and the rock formations, we can assume that  
644 the solution and minerals are in equilibrium. Secondly, since  $\delta^{34}\text{S}$  varies by relatively low  
645 amounts, the added fluid must have a  $\delta^{34}\text{S}$  value close to the one in the reservoir. The  
646 geochemical modelling shows that  $\delta^{34}\text{S}$  of the mixed fluid is close to +10 ‰ CDT, which seems  
647 to be in coherence with an evaporitic origin of sulfate, like gypsum dissolution (André et al.,  
648 2002; Négrel et al., 2009 ; Malcuit, 2012). That is also consistent with values given in the  
649 literature (Claypool et al., 1980) and it is not very far from the +12.4 ‰ CDT measured on  
650 gypsum crystals sampled in the molasse unit of the Aquitaine Basin (André et al., 2002). For  
651 Fluid 3, the  $^{34}\text{S}$  selected had the same value than in the reservoir, which could indicate a higher  
652 proportion of sulfur coming from sulfide minerals.  $\delta^{18}\text{O}_{\text{SO}_4}$  for Nogaro 2 are close to + 10.5 to  
653 14.6 ‰ with low variations with time, which is consistent with the mixing of sulfate having  
654  $\delta^{18}\text{O}_{\text{SO}_4}$  value close to 14.9 ‰, like the one measured on the gypsum from molasse by André et  
655 al. (2002).

656 For boron, the proposed  $\delta^{11}\text{B}$  values were on the order of -3.2 ‰ for Fluid 2 and +12 ‰ for Fluid  
657 3. During this study, a new lab experiment was conducted to identify the potential origin of this  
658 boron. We did not identify any boron-bearing mineral formally among the primary minerals in the  
659 aquifer or in the molasse aquitard. Therefore, rock samples from cuttings and cores sampled at  
660 the top of the aquifer (sampled in a neighbouring well drilled recently) were analysed (XRD  
661 analysis, micro-probe and more) and laboratory tests were carried out to dissolve these  
662 samples. The experiments consisted of dissolving 10 g of crushed material (cuttings) in 100 mL  
663 of water and measuring, after one month, the concentrations of major and trace elements in the  
664 aqueous solution. The experiments were carried out at a temperature of 38°C and atmospheric  
665 pressure. We studied twelve samples from different geological horizons (molasse aquitard and  
666 Lussagnet sands aquifer). After one month, analysis of the water phase showed quite large  
667 disparities between the samples. Essentially, at a depth of 610 m, i.e. in the heart of the  
668 Lussagnet Sands aquifer, for which the depth ranges between 550 m and 650 m, the  $\delta^{11}\text{B}$  value  
669 is similar to that used for the geochemical simulations (Figure 9).



670  
 671 Figure 9 – Boron concentration and  $\delta^{11}\text{B}$  values in the aqueous phase resulting from the lab  
 672 experiments on the dissolution of cuttings sampled at different depths from a well located near  
 673 the Nogaro 2 well. The top of the Lussagnet sands aquifer starts at a depth of 550 m. The grey-  
 674 shaded zone indicates the molasse unit, which overlies the Lussagnet sand aquifer.

675  
 676 Because of the low  $\delta^{11}\text{B}$  values identified in the Lussagnet sand aquifer (between -3.15 and  
 677 +2.00 ‰), it could be inferred that boron may come from the alteration of silicates. Indeed, the  
 678 alteration of silicate minerals by waters gives low  $\delta^{11}\text{B}$  values, ranging between -10 and +10 ‰  
 679 (Barth, 2000; Pennisi et al., 2000; Casanova et al., 2002; Négrel et al., 2002 ; Lemarchand and  
 680 Gaillardet, 2006; Millot et al., 2007; Clauer et al., 2018). As shown in Figure 10, this value is  
 681 also consistent with the end-member of silicates identified by Négrel et al. (2009). The boron  
 682 content of Fluid 2 could be explained by the alteration of the silicate sands of Lussagnet and  
 683 this fluid could mix with the water initially present in the Baliros sands Formation exploited at  
 684 Nogaro 2. During the second modelled cycle, the added Fluid 3 had a slightly higher  $\delta^{11}\text{B}$  value  
 685 at +12 ‰. Literature data show that the  $\delta^{11}\text{B}$  value of evaporites ranges between +15 up to +35  
 686 ‰ according to the evaporation level of the brines (Swihart et al., 1986; Vengosh et al., 1992;  
 687 Liu et al., 2000). Figure 10 confirms the potential evaporitic origin of this boron. This value is  
 688 also close to the mixing line between clays and evaporites calculated by Négrel et al. (2009).  
 689 Therefore we assumed that during this second cycle the boron dissolved in Fluid 3 comes from  
 690 the molassic aquitard, where evaporitic sediments have been identified. Our study seems to  
 691 confirm that the top of the productive part of the aquifer and potentially the molasse could be  
 692 two sources of elements that could feed the exploited part of the aquifer (Baliros sands  
 693 Formation) according to pressure conditions in the reservoir.



694

695 Figure 10 – Variations of  $\delta^{11}\text{B}$  versus the boron concentrations in the waters from Nogaro 2,  
 696 Eauze and Demu. Fluids 1, 2 and 3 correspond to the fluids used for the geochemical  
 697 calculations. End-members (carbonate, evaporite, clays and silicates) and mixing lines are  
 698 issued from Négrel et al. (2009).

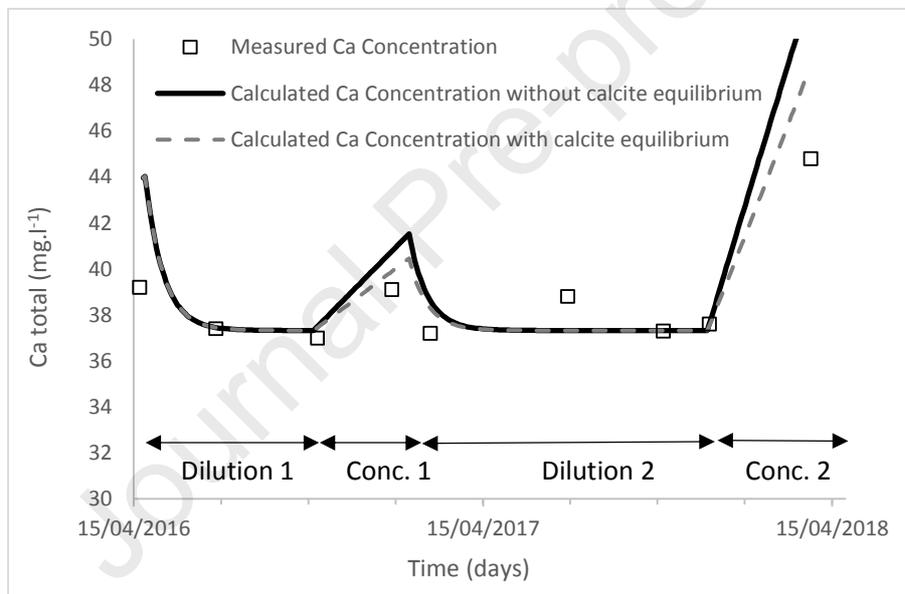
699

700 These potential contributions from the overlying molassic horizons had already been assumed  
 701 by André (2002). Indeed, the upper formation contains gypsum, identified in cuttings. The upper  
 702 aquitard would therefore be a sulfate reserve and sulphur could be transferred into the  
 703 reservoir. We did not investigate the exact transfer mechanisms responsible for the variations of  
 704 certain elements without impacting the concentration of the other elements in detail. Convection  
 705 and/or diffusion are potential processes to explain the seasonal fluctuations (Atteia et al., 2005).  
 706 A sensitive hydrogeologic analysis coupled with the chemical hypothesis defined in this study  
 707 could help to better characterize them. We can however observe from these chemical  
 708 simulations that the mixing proportions differ between the dilution and the concentration phases.  
 709 During the dilution phase, the amounts added every day are relatively high, whereas during the  
 710 concentration phase the daily amounts are very low. Interpreting this difference is tricky since  
 711 only the mixing processes are used in this study without any hydraulic constraints. However,  
 712 one interpretation could be that two processes are in competition. On one side, we can suppose  
 713 that the dilution phase could be assimilated to a hydraulic process with a high renewal rate of  
 714 the aquifer water (or a low resident time). On the other side, the concentration phase could  
 715 correspond to a process with a longer resident time favouring the mixing of the aquifer water  
 716 with a concentrated solution. Though this study helps us to understanding of the chemical

717 variations, it also underlines that the aquifer should not be considered as a single horizon and  
 718 that local structural and hydrogeological heterogeneities may explain vertical differentiation in  
 719 the aquifer.

720 This does raise a question regarding these geochemical simulations. Since it is assumed that  
 721 the mixed concentrated fluids are enriched in sulfate and in equilibrium with gypsum, the  
 722 calcium concentration in solution should increase (Figure 11). But the sulfate increase does not  
 723 follow the same trend as that of calcium (and/or magnesium). Figure 16 clearly shows that the  
 724 measured calcium concentrations are lower than the calculated values. This could mean that  
 725 calcium (and/or magnesium) is controlled by another mechanism.

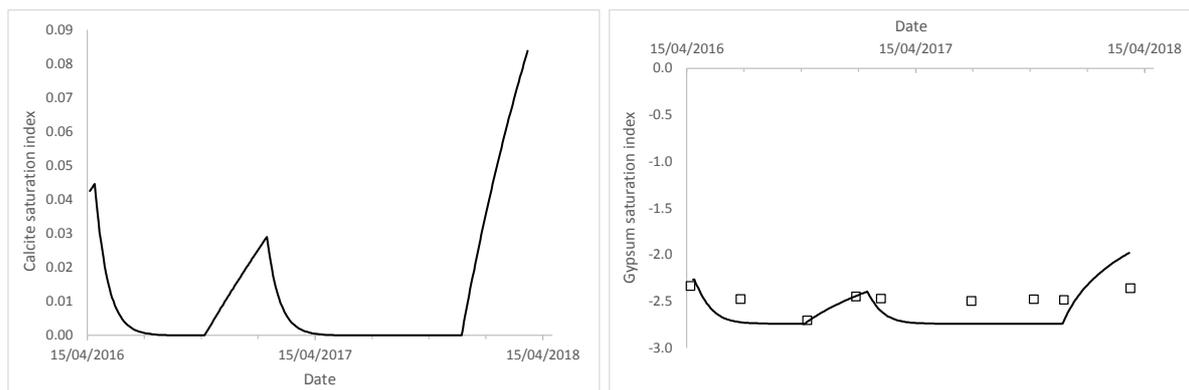
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727

728 **Figure 11 – Variation in calcium concentration. Curves are results of two simulations**  
 729 **(with and without maintaining calcite equilibrium) whereas symbols are calcium**  
 730 **concentration measured during quarterly samplings**

731 During the addition of concentrated fluids (Fluids 2 and 3), calcium is added in a solution (Fluid  
 732 1) initially in equilibrium with calcite. Then the saturation indices of calcite increases and the  
 733 carbonate mineral becomes over-saturated, whereas the gypsum remains under-saturated  
 734 (Figure 12).



735  
 736 **Figure 12 – Variation of the simulated saturation indices of calcite (left) and gypsum**  
 737 **(right) during the mixing of Fluid 1 with Fluids 2 and 3. Lines are results of simulations**  
 738 **whereas symbols are saturation indices calculated from chemical compositions of**  
 739 **waters measured during quarterly samplings**

740 Because of calcium's high kinetic reactivity, this mineral is often assumed to be in equilibrium  
 741 with the solution. A new geochemical run was then performed assuming calcite equilibrium and  
 742 imposing a CO<sub>2</sub> partial pressure of 10<sup>-2</sup> atm during the mixing. Under this condition, the calcium  
 743 concentration in solution is controlled by calco-carbonic equilibrium and secondary calcite is  
 744 precipitating in the reservoir. By imposing this constraint to the chemical model, Figure 11  
 745 shows that the calcite precipitation controls and decreases the calcium content in the solution  
 746 and numerical results are more coherent with measured data. Moreover, it is admitted that light  
 747 isotopes concentrate in the least dense phase, i.e. in the liquid phase instead of the solid phase  
 748 (Allègre and Michard, 1973 ; Hoefs, 1997; Couchoud, 2008). Consequently, <sup>13</sup>C precipitates in  
 749 priority under calcite, the solution is enriched with the light isotope and the δ<sup>13</sup>C value  
 750 decreases. It corresponds to the observations in Nogaro 2 since sulfate concentration and δ<sup>13</sup>C  
 751 are anticorrelated : during the concentration phase, sulfate increases, calcite precipitates and  
 752 δ<sup>13</sup>C decreases (Figure 6).

## 753 6 - Conclusions

754 The 2-year monitoring of concentrations of major and trace elements and stable and radioactive  
 755 isotopes confirms the cyclical and seasonal variations in sulfate (between 10 and 40 mg.l<sup>-1</sup>) as  
 756 well as variations in sulfur-34 of sulfate (between +6.5 and +8.5 ‰) at the Nogaro 2 well.  
 757 Though sulfate variations were known, additional variations in boron (total concentration and  
 758 isotope) and carbon (<sup>13</sup>C and <sup>14</sup>C) contents have been also highlighted by these new  
 759 campaigns. However, given the very small activity in <sup>14</sup>C, it has been difficult to conclude on the  
 760 origin of the measured variations (geochemical processes, water mixtures, uncertainties related

761 to samples and analyses, for instance). Further study of this parameter could be considered, in  
762 particular to define the uncertainty associated with abstractions and analyses.

763 In terms of interpretations, geochemical modelling based on water mixtures has revealed  
764 concentration processes in relation with mixtures of sulfate and boron-enriched waters and  
765 dilution stages, corresponding to mixes between water from the reservoir and water coming  
766 from other origins. While the geochemical models make it possible to properly restore both  
767 sulfate and boron concentrations in the water (as well as the  $\delta^{34}\text{S}$  and  $\delta^{11}\text{B}$  values), this  
768 approach must be considered exploratory in order to propose mixing end-members. Ideally, this  
769 study should be supplemented by a more accurate analysis of the minerals present at the site  
770 (in the reservoir and in the layers both beneath and overlying). This mineral study would allow  
771 us to define more precisely the phases bearing sulfur and boron and to characterize them  
772 (especially in terms of isotopic content). The geological and mineralogy study we carried out  
773 confirms that in the Nogaro 2 zone sulfur may have two origins: gypsum, which is generally  
774 present in the molassic aquitard, and pyrite, present in the reservoir. However, it has not been  
775 possible to characterize the sulfur of these pyrites precisely, especially in terms of isotope. The  
776 small amount of pyrite and the coating of the grains by quartz deposits prevented any  
777 purification and isotopic analysis. However, these characterizations would be necessary to  
778 determine the origin of sulfate in the waters, especially during peak phases.

779 This study therefore provides important elements for understanding the processes responsible  
780 for variations in sulfate concentration in waters from Nogaro 2. It appears that these variations  
781 are probably related to coupled hydrodynamic and geochemical processes and that only a finer  
782 characterization of the end-members (origin of sulfur and boron, phases bearing these  
783 elements, stock/reserve of these elements, etc.) and exchanges between the different parts of  
784 the reservoir (and the aquitards) will help to understand the mechanisms occurring at this  
785 borehole. A coupled hydrogeological and chemical approach will also be needed to better  
786 understand these processes.

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## Appendix

Table A-1: Physico-chemical parameters of the waters measured on site

Well	Date	Conductivity ( $\mu\text{S/cm}$ )	pH	T°C	O <sub>2</sub> (%)	O <sub>2</sub> (mg/l)	Eh <sub>measured</sub> (mV)	Eh <sub>corrected</sub> / ENH (mV)
NOGARO 2	19/04/2016	325	7.2	51	42	2.35	-209	-19
	18/07/2016	296	7.13	50.9	3.3	0.19	-284	-94
	04/10/2016				<i>Not measured</i>			
	10/01/2017	347	7.17	48.7		0.65	-199	-7
	21/03/2017	384	7.75	42.0	72.8	4.84	-129	68
	27/06/2017	328	7.55	49.1	20.2	1.18	-93	98
	03/10/2017	296	7.48	47.2	39.7	2.29	-112	81
	14/12/2017	338	7.71	46	67.8	4.04	-122	72
01/03/2018	365	7.85	44.5	82.5	4.77	94	289	
EAUZE	19/04/2016	308	7.32	36.4	3.2	0.21	-169	30
	18/07/2016	307	7.14	36.4	5.9	0.4	-215	-14
	04/10/2016				<i>Not measured</i>			
	10/01/2017	333	7.4	31.5		0.53	-165	39
	21/03/2017	325	7.73	31.8	48.2	3.76	-80	124
	27/06/2017	330	7.75	35.5	58.8	4.01	53	254
	03/10/2017	319	7.23	27.8	53.9	4.2	135	342
	14/12/2017	326	7.65	32.0	38.5	2.78	18.4	222
01/03/2018	316	7.5	34.9	40.5	2.71	95	297	
DEMU	19/04/2016	298	7.38	48.1	29.1	1.83	-187	5
	18/07/2016	293	7.14	53.9	56.8	3.10	-219	-31
	04/10/2016				<i>Not measured</i>			
	10/01/2017	326	7.25	53.2		0.10	-198	-10
	21/03/2017	323	7.44	46.6	14.3	0.91	-145	48
	27/06/2017	325	7.46	48.0	15.8	0.88	-125	67
	03/10/2017	296	7.21	53.0	3.0	0.16	-211	-22
	14/12/2017	326	7.45	49.0	15.0	0.92	-173	18
01/03/2018	462	7.25	48.0	12.8	0.73	52	244	

**Table A-2: Chemical composition of major elements (Concentrations in mg.l<sup>-1</sup>) and calculated molar ratio**

Date	Well	Ca	Mg	K	Na	SO <sub>4</sub>	HCO <sub>3</sub>	Cl	SiO <sub>2</sub>	<i>Ca + Mg</i>	<i>Ca + Mg</i>	<i>Na + K</i>
										<i>SO<sub>4</sub></i>	<i>Cl</i>	<i>Cl</i>
Apr.-16	NOGARO 2	39.2	5.2	5.2	14.5	24.2	155	7.5	23.1	4.74	11.30	3.61
	EAUZE	35.4	5.1	5.7	15.7	19.5	153	6.5	17.4	5.39	11.96	4.52
	DEMU	32.2	4.5	5.8	17.5	6.8	160	7.9	24.5	13.98	8.90	4.09
Jul.-16	NOGARO 2	37.4	4.5	5.3	14.1	10.1	153	7.6	24.3	10.65	10.46	3.50
	EAUZE	36.0	5.3	5.8	16.4	18.8	150	6.5	18.9	5.71	12.21	4.70
	DEMU	33.7	4.6	5.9	18.2	7.0	157	7.9	26.3	14.15	9.27	4.23
Oct.-16	NOGARO 2	37	4.6	5.7	14.6	10.5	153	7.7	24.3	10.19	10.27	3.60
	EAUZE	36.8	5.6	6.2	17.0	23.9	149	6.6	18.9	4.62	12.38	4.83
	DEMU	32.7	4.6	6.3	18.9	6.3	158	8.0	25.7	15.34	8.94	4.36
Jan.-17	NOGARO 2	39.1	4.9	5.5	15.2	17.9	152	7.8	24.1	6.32	10.73	3.65
	EAUZE	35.8	5.4	6.0	16.6	19.8	148	6.7	18.4	5.42	11.84	4.64
	DEMU	33.2	4.6	6.0	19.0	6.8	155	8.1	25.8	14.39	8.93	4.29
Mar-17	NOGARO 2	37.2	4.7	5.6	14.9	14.9	154	7.5	24.6	7.24	10.64	3.74
	EAUZE	35.3	5.3	5.9	16.6	19.8	151	6.3	18.8	5.34	12.40	4.92
	DEMU	33.1	4.7	6.0	18.6	6.4	159	7.8	26.5	15.31	9.29	4.38
Jun-17	NOGARO 2	38.8	4.4	5.5	14.5	10.7	149	7.6	25.4	10.33	10.75	3.60
	EAUZE	37.3	5.1	6.0	16.7	19.7	145	6.5	19.5	5.57	12.48	4.80
	DEMU	34.5	4.4	6.2	18.7	6.9	152	7.9	26.8	14.52	9.38	4.37
Oct.-17	NOGARO 2	37.3	4.5	5.2	13.5	10.6	154	7.7	23.1	10.12	10.31	3.32
	EAUZE	36.6	5.3	5.8	15.6	20.2	151	6.7	17.3	5.39	12.01	4.38
	DEMU	33.4	4.6	5.9	17.5	6.6	158	8.1	24.5	14.90	8.98	4.00
Dec.-17	NOGARO 2	37.6	4.5	5.6	14.1	11.2	153	7.7	24.3	9.64	10.38	3.49
	EAUZE	37.1	5.3	6.0	16.4	23.2	149	6.5	19.1	4.74	12.51	4.73
	DEMU	33.2	4.6	6.1	18.0	6.4	157	8.0	26.3	15.29	9.05	4.17
Mar-18	NOGARO 2	44.8	6.3	5.7	16.3	46.7	154	7.6	24.9	2.84	12.89	3.99
	EAUZE	35.4	5.3	5.9	15.9	20.4	151	6.7	19.0	5.19	11.69	4.46
	DEMU	32.8	4.5	6.0	17.8	7.1	158	8.1	26.5	13.59	8.81	4.06

**Table A-3: Concentrations of trace elements**

Date	Well	Al µg/l	B µg/l	Ba µg/l	F mg/l	Fe mg/l	Li µg/l	Mn µg/l	Sr µg/l	Br µg/l
Apr.-16	NOGARO 2	1.13	43.9	120	0.2	0.208	11.20	7.8	496	< LQ
	EAUZE	0.66	42.2	95	0.2	0.108	10.20	12.3	466	81
	DEMU	1.61	42.3	113	0.2	0.232	13.80	13.4	457	54
Jul.-16	NOGARO 2	1.02	24.3	111	0.2	0.225	9.38	6.4	438	<50
	EAUZE	0.58	42.5	97	0.2	0.104	10.20	11.9	475	<50
	DEMU	1.40	43.7	112	0.2	0.210	13.90	12.1	468	<50
Oct.-16	NOGARO 2	1.92	24.7	104	0.2	0.184	9.88	5.2	455	145
	EAUZE	1.16	47.6	90	0.2	0.109	11.60	12.6	480	208
	DEMU	1.05	47.2	105	0.2	0.265	15.20	19.4	457	99
Jan.-17	NOGARO 2	0.6	29.3	91.4	0.2	0.309	8.27	10.9	436	< LQ
	EAUZE	0.56	35.4	80.5	0.2	0.349	8.97	13.9	445	< LQ
	DEMU	0.73	33.3	93.1	0.2	0.343	10.9	12.7	434	< LQ
Mar.-17	NOGARO 2	NM	33.7	109	0.2	0.192	11.2	6.63	442	157
	EAUZE	NM	45.1	91.7	0.2	0.191	11.2	17.1	458	147
	DEMU	NM	46.1	109	0.2	0.122	15.3	18.6	440	129
Jun.-17	NOGARO 2	1.52	25.4	110.00	0.1	< LQ	9.86	6.4	433	29.0
	EAUZE	1.90	46.6	111.00	0.2	0.173	14.5	12.6	473	34.6
	DEMU	0.61	46.0	95.60	0.2	< LQ	10.5	12.4	470	27.1
Oct.-17	NOGARO 2	1.52	22.6	112.00	0.1	0.2	10.1	5.52	414	67.1
	EAUZE	1.47	41.5	96.20	0.2	< 0.02	10.7	12.6	462	44.7
	DEMU	1.46	42.3	113.00	0.2	0.376	14.4	17.2	450	49.0
Dec.-17	NOGARO 2	1.90	25.7	105.00	0.1	0.05	10.4	5.51	309	28.6
	EAUZE	0.90	43.4	86.60	0.2	< 0.02	10.5	11.5	330	24.8
	DEMU	1.43	42.5	106.00	0.2	0.352	14.0	15.0	319	34.0
Mar.-18	NOGARO 2	1.95	79.5	101.87	0.2	0.027	14.71	8.83	570	30.9
	EAUZE	0.69	44.3	93.93	0.2	0.036	9.51	12.13	455	28.4
	DEMU	2.00	45.1	109.36	0.2	0.214	14.68	11.84	449	36.4

< LQ : lower to quantification limits ; NM : not measured

**Table A-4:  $^2\text{H}$  and  $\delta^{18}\text{O}$  of water molecule**

	$\delta\text{D}$ (‰ vs SMOW) (+/- 0.8 ‰)				$\delta^{18}\text{O}$ (‰ vs SMOW) (+/- 0.1 ‰)			
	Apr-16	Jul-16	Oct-16	Jan-17	Apr-16	Jul-16	Oct-16	Jan-17
NOGARO 2	-54.3	-54.7	-54.3	-54.5	-8.5	-8.5	-8.5	-8.5
EAUZE	-52.6	-52.5	-52.7	-53.0	-8.3	-8.3	-8.2	-8.4
DEMU	-52.7	-52.7	-52.6	-53.0	-8.3	-8.3	-8.4	-8.3

**Table A-5:  $^{87}\text{Sr}/^{86}\text{Sr}$  ratio**

	Apr-16		Jul-16		Oct-16		Jan-17	
	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma(\text{m})$	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma(\text{m})$	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma(\text{m})$	$^{87}\text{Sr}/^{86}\text{Sr}$	$2\sigma(\text{m})$
NOGARO 2	0.708704	0.000008	0.708712	0.000007	0.708717	0.000007	0.708710	0.000006
EAUZE	0.708698	0.000005	0.708700	0.000006	0.708701	0.000008	0.708700	0.000008
DEMU	0.708781	0.000006	0.708778	0.000009	0.708778	0.000006	0.708774	0.000008

**Table A-6: Isotope concentrations**

Date	Well	$\delta^{13}\text{C}$ ‰ vs PDB ( $\pm 0.1$ )	Act. $^{14}\text{C}$ (pMC)	$\delta^{11}\text{B}$ ‰ (Try 1)	$\pm 2\sigma(\text{m})$ ‰	$\delta^{11}\text{B}$ ‰ (Try 2)	$\pm 2\sigma(\text{m})$ ‰	$\delta^{34}\text{S}$ ( $\text{SO}_4$ ) ‰ vs CDT ( $\pm 0.3$ ‰)	$\delta^{18}\text{O}$ ( $\text{SO}_4$ ) ‰ vs SMOW ( $\pm 0.5$ ‰)
Apr.-16	NOGARO 2	-14.60	$1.8 \pm 0.1$	11.67	0.06	11.49	0.11	8.00	13.5
	EAUZE	-14.60	$1.5 \pm 0.1$	13.97	0.06	13.58	0.08	9.30	12.8
	DEMU	-15.30	$3.2 \pm 0.1$	17.94	0.04	17.70	0.09	15.90	10.2
Jul.-16	NOGARO 2	-14.80	$1.5 \pm 0.1$	17.57	0.07	17.63	0.09	6.80	$10.6 (\pm 0.6 \text{ ‰})$
	EAUZE	-14.30	$0.5 \pm 0.1$	15.23	0.09	15.32	0.06	9.50	$14.1 (\pm 0.6 \text{ ‰})$
	DEMU	-15.50	$1.1 \pm 0.1$	19.47	0.06	19.44	0.11	15.80	10.7
Oct.-16	NOGARO 2	-14.30	$2.0 \pm 0.1$	15.45	0.05	15.83	0.08	$6.80 (\pm 0.4 \text{ ‰})$	10.4
	EAUZE	-14.00	$0.1 \pm 0.1$	13.68	0.06	13.31	0.08	9.50	12.3
	DEMU	-15.30	$1.5 \pm 0.1$	19.03	0.05	18.81	0.08	18.40	11.5
Jan.-17	NOGARO 2	-15.00	$1.3 \pm 0.0$	10.95	0.09	11.23	0.05	8.10	13.0
	EAUZE	-14.80	< 0.44	14.65	0.08	14.28	0.06	10.00	13.0
	DEMU	-15.70	$0.9 \pm 0.0$	18.67	0.05	18.61	0.07	17.90	11.0
Mar.-17	NOGARO 2	-15.20	$1.7 \pm 0.0$	9.64	0.06	9.89	0.04	7.00	11.00
	EAUZE	-15.30	$0.8 \pm 0.0$	12.80	0.05	12.90	0.04	10.00	12.60
	DEMU	-15.50	$0.8 \pm 0.0$	19.02	0.17	18.84	0.10	17.80	11.40
Jun.-17	NOGARO 2	-14.60	$1.9 \pm 0.0$	16.90	0.18	17.09	0.14	6.50	10.50
	EAUZE	-13.70	$1.4 \pm 0.0$	14.86	0.27	14.66	0.09	9.60	12.60
	DEMU	-15.30	$1.1 \pm 0.0$	18.80	0.07	18.94	0.06	17.10	11.20
Oct-17	NOGARO 2	-13.00	$1.5 \pm 0.0$	17.16	0.03	17.17	0.05	6.60	11.10
	EAUZE	-13.80	$0.9 \pm 0.0$	14.63	0.03	14.25	0.05	9.80	13.30
	DEMU	-14.90	$0.9 \pm 0.0$	18.65	0.04	18.82	0.04	20.00	11.80
Dec-17	NOGARO 2	-13.80	$2.2 \pm 0.0$	15.94	0.04	15.97	0.05	6.70	11.20
	EAUZE	-11.30	$1.7 \pm 0.0$	14.18	0.05	13.98	0.06	9.20	13.40
	DEMU	-14.50	$1.1 \pm 0.0$	18.91	0.10	18.77	0.18	17.80	11.40
Mar-18	NOGARO 2	-13.80	$1.5 \pm 0.0$	7.98	0.05	7.57	0.18	8.20	14.60
	EAUZE	-14.00	$0.6 \pm 0.0$	13.89	0.06	13.76	0.23	9.20	13.20
	DEMU	-15.10	$1.0 \pm 0.0$	18.62	0.05	18.17	0.04	17.90	11.50

< LQ : lower to quantification limits ; NM : not measured

**Table A-7: Saturation indices of minerals calculated with PHREEQC program and THERMODDEM database (Blanc et al., 2012)**

Well	Date	Calcite	Dolomite	Gypsum	Anhydrite	Barite	Strontianite	Quartz	Chalcedony	Montmorillonite (MgCa)	Illite (Al)	Log pCO <sub>2(g)</sub>
NOGARO 2	19/04/2016	-0.05	-0.40	-2.27	-2.19	-0.24	-1.66	0.01	-0.25	-0.72	-0.99	-1.84
	18/07/2016	-0.14	-0.61	-2.65	-2.57	-0.64	-1.78	0.04	-0.22	-0.68	-0.89	-1.77
	04/10/2016	-0.28	-0.90	-2.64	-2.57	-0.64	-1.90	0.05	-0.21	-0.09	0.26	-1.65
	10/01/2017	-0.12	-0.58	-2.40	-2.34	-0.46	-1.77	0.06	-0.21	-0.93	-1.36	-1.83
	21/03/2017	0.34	0.30	-2.52	-2.53	-0.39	-1.24	0.14	-0.13	NC	NC	-2.46
	27/06/2017	0.25	0.13	-2.62	-2.56	-0.61	-1.40	0.07	-0.19	-0.44	-0.90	-2.22
	03/10/2017	0.16	-0.05	-2.64	-2.60	-0.58	-1.49	0.05	-0.21	-0.42	-0.68	-2.15
	14/12/2017	0.36	0.35	-2.62	-2.59	-0.57	-1.40	0.09	-0.18	-0.23	-0.61	-2.39
	01/03/2018	0.52	0.73	-1.98	-1.96	0.02	-1.04	0.11	-0.15	-0.11	-0.65	-2.55
EAUZE	19/04/2016	-0.19	-0.74	-2.44	-2.50	-0.27	-1.69	0.06	-0.22	-0.60	-0.39	-2.06
	18/07/2016	-0.37	-1.09	-2.44	-2.50	-0.27	-1.87	0.10	-0.18	-0.45	-0.12	-1.89
	04/10/2016	-0.03	-0.41	-2.34	-2.42	-0.19	-1.53	0.11	-0.17	-0.03	0.30	-2.27
	10/01/2017	-0.19	-0.77	-2.43	-2.54	-0.27	-1.69	0.14	-0.14	-0.27	0.01	-2.19
	21/03/2017	0.14	-0.10	-2.44	-2.54	-0.21	-1.34	0.14	-0.13	NC	NC	-2.51
	27/06/2017	0.22	0.05	-2.42	-2.48	-0.19	-1.29	0.12	-0.16	0.18	0.40	-2.53
	03/10/2017	-0.40	-1.23	-2.42	-2.56	-0.13	-1.87	0.16	-0.12	0.69	1.90	-2.04
	14/12/2017	0.08	-0.25	-2.36	-2.46	-0.18	-1.57	0.15	-0.13	-0.05	0.11	-2.44
	01/03/2018	-0.04	-0.44	-2.42	-2.49	-0.23	-1.54	0.11	-0.16	-0.39	-0.34	-2.26
DEMU	19/04/2016	0.03	-0.24	-2.89	-2.83	-0.77	-1.51	0.07	-0.19	-0.29	-0.41	-2.02
	18/07/2016	-0.12	-0.50	-2.83	-2.73	-0.82	-1.70	0.04	-0.22	-0.53	-0.72	-1.75
	04/10/2016	-0.08	-0.41	-2.89	-2.80	-0.88	-1.66	0.04	-0.22	-0.76	-1.09	-1.81
	10/01/2017	-0.03	-0.32	-2.86	-2.76	-0.90	-1.63	0.04	-0.22	-1.05	-1.67	-1.87
	21/03/2017	0.07	-0.15	-2.91	-2.87	-0.80	-1.49	0.12	-0.14	NC	NC	-2.10
	27/06/2017	0.11	-0.11	-2.85	-2.80	-0.84	-1.45	0.11	-0.15	-0.88	-1.60	-2.13
	03/10/2017	-0.06	-0.39	-2.87	-2.77	-0.83	-1.65	0.02	-0.24	-0.60	-0.79	-1.82
	14/12/2017	0.11	-0.06	-2.90	-2.84	-0.83	-1.60	0.09	-0.17	-0.36	-0.68	-2.10
	01/03/2018	-0.10	-0.50	-2.86	-2.81	-0.76	-1.66	0.11	-0.16	0.09	0.24	-1.90

\*NC : Not Calculated

**Highlights :**

- Deep confined aquifers can be submitted to heavy and seasonal pressure variations
- Cyclic variations of sulfate and boron are observed over an extended area
- Concentration and isotope ratios of the two elements vary in accordance with each other
- Geochemical modelling based on water mixes fits the field observations
- Observations and simulations confirm water and mass fluxes within deep aquifers

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**Declaration of interests**

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

The authors declare the following financial interests/personal relationships which may be considered as potential competing interests:

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