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Characterization and sampling of a deep and heterogeneous aquifer – An application to the Paleocene – Eocene aquifer in the Aquitaine basin, France

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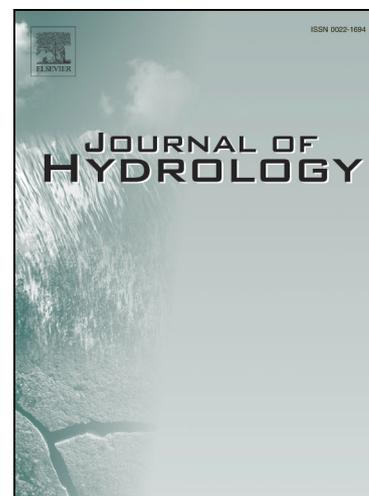
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1 **Characterization and sampling of a deep and heterogeneous aquifer – An application to the**
2 **Paleocene – Eocene aquifer in the Aquitaine basin, France**

3

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11 **Abstract**

12 Groundwater sampling in boreholes has been carried out for decades according to well-established
13 protocols and regulations. An important requirement in this context is the need to purge the
14 borehole prior to any sampling action, the volume of the purge being adapted to the water flow and
15 the regulatory context. Contaminated site investigations have introduced the concept of water
16 column heterogeneity in the screened section of boreholes, which also occurs in some
17 uncontaminated boreholes or in long-screened boreholes. Specific guidelines and practices were
18 thus introduced, in particular the concept of discrete sampling. This type of sampling can be
19 advantageously used in deep boreholes, provided that there is some renewal of water at the screens
20 or the perforated intervals. The present study aims to take a step forward in the characterization of
21 deep boreholes set up in the Aquitaine basin in France, by defining a protocol for relatively short
22 boreholes (depth < 170 m) and applying it to much deeper boreholes, formerly drilled for oil and gas
23 exploration (sampling up to 1035 m deep). Acquisitions were performed to better characterize water
24 chemistry, including some isotope considerations. They were based on physico-chemical logging and
25 endoscopic inspections where technically possible. After a review of the information provided by the
26 investigations on the characterization of the Paleocene – Eocene aquifer in southwestern France, a
27 methodology is proposed to make sampling in deep boreholes with low-yield more reliable, by
28 combining the abstraction of a reduced water volume and the use of a downhole sampling system.

29

30 **Keywords**

31 Deep borehole – downhole sampling – water sample representativeness

32 1. Introduction

33 Water sampling, and especially groundwater sampling in boreholes, which is the focus of this study,
34 has been performed for decades either for regulatory purposes (water drinking regulations) or for a
35 better knowledge of aquifers. Best practice guidelines were defined early (*e.g.* Rainwater and
36 Thatcher, 1960) and have evolved regularly since then, based on feedbacks from field operators and
37 regulators (*e.g.* Brown *et al.*, 1970; Wood, 1976; Gibb *et al.*, 1981; Lallemand-Barrès, 1993). In
38 Europe, the focus was placed on best practices thanks to the first regulatory framework for
39 groundwater in the end of the 1970's (Directive 80/68/EC). Subsequent directives, namely the Water
40 Framework Directive (WFD) in 2000 (Directive 2000/60/EC) and its daughter directive on
41 groundwater in 2006 (Directive 2006/118/EC), have completed the corpus. These directives aimed to
42 achieve good (quantitative and chemical) status for water bodies supposedly by 2015. As a result, a
43 large literature is available worldwide to help in better sampling and thus characterizing
44 groundwaters (*e.g.* OFEV, 2003; USGS, 2006; Duncan *et al.*, 2007; Ministère du Développement
45 Durable, de l'Environnement et des Parcs du Québec, 2011; Ghestem *et al.*, 2017). Moreover, most
46 of the guidelines are in accordance with those from the ISO standards, and more specifically the 5667
47 standard and its parts (ISO 5667-11, 2009).

48 One of the main principle exposed in these guidelines is the need of purging a borehole prior to any
49 sampling (Barcelona and Helfrich, 1986). This is because the water in the screened section is
50 renewed due to flow patterns but the water above the screened section is not and is therefore not
51 representative of the groundwater (US-EPA, 1999). In most cases, the flow pattern in the screened
52 section is lateral and directly related to that of the aquifer as a function of its transmissivity, but well-
53 bore flow (vertical mixing) may occur especially in open holes and boreholes with long or multiple
54 screened sections (USGS, 2006). Additionally, water sampling from boreholes that cannot produce a
55 continuously pumped sample or boreholes in which water-level recovery takes longer than 24 hours
56 after being pumped is not recommended (USGS, 2006). Apart from these cases, the general rule is to
57 evacuate at least one volume of water in the well casing, and preferably three to five volumes, to get

58 a representative sample (US-EPA, 1999). Depending on the flowrate of the pump, the pump intake
59 will be located either above the screened section (high flow-rate pump) or in the screened section
60 (low flow-rate pump) in order to avoid damaging screens and displacing the gravel-pack.

61 Besides these guidelines, several exceptions to the rule exist, for example on contaminated sites
62 where volatile organic compounds may be monitored (Barcelona *et al.*, 1994) or in open holes in
63 fractured bedrock (Shapiro, 2002). In such cases, other pumping strategies may be required because
64 sampling results have been demonstrated to be sensitive to well-purging rate, the volume of
65 abstracted water and the disturbance created by downhole pumping (Gibb *et al.*, 1981). From an
66 assumption of homogeneity of the water column in the screened section, the view progressively
67 shifted to the highlight of the role of heterogeneity in the water column, as in geological logs (Puls
68 and Barcelona, 1996). This led to the development of low-flow purging techniques (Puls and Powell,
69 1992), which have demonstrated their usefulness in small-diameter boreholes equipped with short-
70 screened intervals (Barcelona *et al.*, 1994, 2005), and to the use of inflatable packers where screened
71 intervals are long or in open holes (Smellie and Wikberg, 1991; Shapiro, 2002). Later on, other
72 systems for discrete sampling at low-flow have been designed: the Model 401 Waterloo Multilevel
73 System (Solinst®; Cherry and Johnson, 1982), the Continuous Multichannel Technology system
74 (Solinst®; Einarson and Cherry, 2002), the Water FLUTE™ (Flexible Liner Underground Technologies,
75 Ltd. Co; Cherry *et al.*, 2007) or the Westbay MP system (Westbay Instruments Inc.; Black *et al.*, 1986).

76 Such sampling systems are mostly used in shallow boreholes (<100 m) and benefit from a large
77 number of sampling points allowing discrete and precise characterization of the water column
78 (Chapman *et al.*, 2015). Nevertheless, some of these systems have a far larger investigation depth
79 (up to 1200 m for the Westbay system; Einarson, 2005). These systems appear to be relevant for site-
80 specific borehole monitoring, but they require dedicated borehole completions. In the case of pre-
81 existing boreholes, implementing such systems may turn out to be costly (*i.e.* if there is no need of
82 permanent or regular monitoring of the aquifer), provided the borehole diameter is adapted
83 (Einarson, 2005).

84 When the depth of investigation has to be further extended, the use of multi-ports systems is less
85 common, with the exception of the U-tube sampling system, a positive fluid displacement pump
86 using a high pressure gas drive and valves, designed for Carbon Capture and Storage applications and
87 operated through a dedicated completion (Freifeld *et al.*, 2005). The U-tube system was deployed
88 down to 2870 m (Conaway *et al.*, 2016) and nested deployments allowing multi-level sampling are
89 also reported (Boreham *et al.*, 2011). If the sampling system has to be retrievable, sampling may rely
90 on downhole (in-situ) sampling systems. The use of electric submersible pumps and sampling
91 systems used in the oil industry is not considered for cost reasons (Crombie *et al.*, 1998; Wolff-
92 Boenisch and Evans, 2014). Downhole sampling systems are namely positive displacement samplers,
93 vacuum samplers and flow-through samplers (Wolff-Boenisch and Evans, 2014). These samplers need
94 to be driven down to the desired sampling depth with a wireline, and valve mechanisms allow fluid
95 sampling by means of pressure differential (positive displacement and vacuum samplers) or not
96 (flow-through sampler).

97 We present here the results of investigations performed on some deep boreholes of the Aquitaine
98 Basin, in southwest France, between 2014 and 2018. The acquisitions were not all done under the
99 same project so that focus and outcomes may differ from one well to the other. Deep sampling was
100 always performed, to characterize the water chemistry (characterization of the gas contents is not
101 presented here). In some cases, physico-chemical logging was performed prior the investigations, to
102 assess the evolution of parameters along the water column in boreholes that are not used for water
103 supply. Some pumping phases were also done in selected boreholes, to evaluate if relevant deep
104 sampling can be performed without any well-bore purging or not. Though the data were acquired to
105 improve the knowledge on deep aquifers in this large sedimentary basin, they are mainly used to
106 define an approach to get reliable estimates of the chemistry of deep aquifers and therefore to set a
107 methodological approach for further investigations in similar boreholes.

108

2. Hydrogeological settings and boreholes description

The surveyed boreholes are located in the southern part of the Aquitaine basin. Two boreholes (Labruguière, LBG and Valdurenque, VLD) are located close to the eastern border of the basin, and were drilled in 1990 for water monitoring down to respectively 177 and 129 m depth (Figure 1). They are equipped with stainless steel screened sections so the water flow is supposed to be better constrained. The three other boreholes are old and deep wells initially drilled for oil exploration in the second half of the XXth century (André *et al.*, 2005). These wells were generally drilled to some kilometers depth. They were converted later into groundwater monitoring boreholes by sealing their lower parts and by perforating the casing at a selected depth interval (Roche, 1977). For example, Polastron (PO-101) well was drilled in 1957 down to 2751 m depth and is now perforated at only 818.5-828.5 m depth (Figure 1), *i.e.* there is no more water flow from horizons deeper than 828.5 m (obstruction at 951.4 m depth). Muret-104 (MU-104) well is perforated at 1031.6-1040 m depth and Lacquy (LC-101) well is perforated at 435-445 m depth.

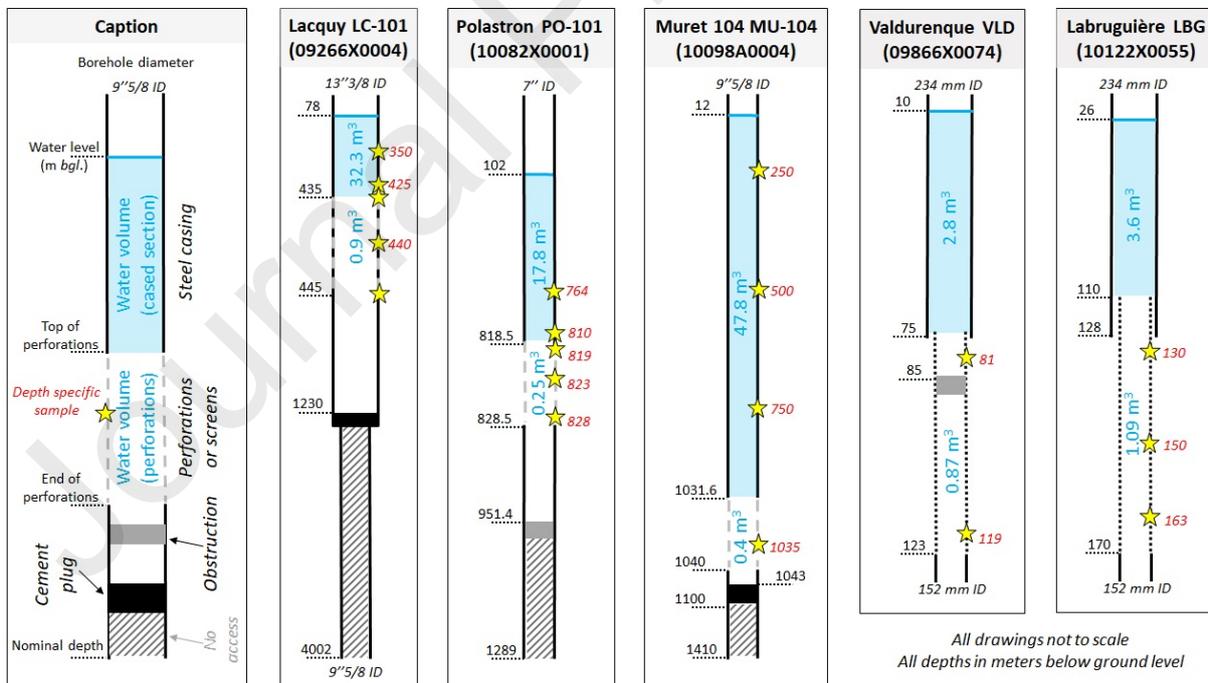


Figure 1: boreholes geometry with location of the screened sections or the perforations; the volumes reported in blue correspond to water volumes in the selected casing section; the yellow stars indicate the depths of sampling with GOG in this study.

126

127 In the former oil exploration wells (PO-101, MU-104 and LC-101) water flows locally through
128 perforations in the steel casing but the water flow is less constrained than in screened intervals
129 because perforations were made using isolated explosive charges and the connectivity to the aquifer
130 can be variable from one borehole to the other. Nevertheless, their long-term water table
131 monitoring suggests that some hydraulic connectivity to the aquifer remains. Last, as the casing
132 material is steel, sampling depths have to be considered with care regarding the potential influence
133 of corrosion on water quality if water is not renewed (Pohlmann and Alduino, 1992).

134 The studied boreholes tap one of the major aquifer system of the Aquitaine basin, the FG082 aquifer
135 (ADES, 2020) formed by sands, limestones and dolomites of Paleocene to Eocene age. This aquifer is
136 one of the main water resources in the basin and is used for several applications over its wide extent:
137 drinking water, irrigation, thermal and hydrothermal resources and gas storage in aquifer (André *et*
138 *al.*, 2002, 2005; Brenot *et al.*, 2015). Most of this FG082 aquifer (99.3% of its surface) is confined. This
139 aquifer has highly variable chemical characteristics in relation with a variety of lithologies and a large
140 range of depth (from tens of meters to several hundreds). This Paleocene to Eocene aquifer encloses
141 indeed aquifer formations from Danian (limestone) and Selandian (sandstone and gravel sands) ages,
142 which are tapped below 1500 m depth in the center of the basin, and aquifer formations from the
143 Ypresian to Lutetian age, which are tapped by LC-101, PO-101, MU-104 and LBG at lower depths
144 (Figure 1). The Ypresian to Lutetian aquifer is also called the infra-molassic sand aquifer and is
145 formed by sands and gravels with possible minor intercalations of sandy clays. Last, the VLD borehole
146 taps slightly younger formations from the Lutetian age (so called “gravel clays”).

147 Little information is known on the hydraulic properties of the deep boreholes tapping the Paleocene
148 – Eocene aquifer – with the exception of water table monitoring data that are not discussed here
149 (SIGES AQI, 2020). On the three deep boreholes, information is available for MU-104 (BSS EAU,
150 2020a) and to a lesser extent for PO-101 (Berard and Sourisseau, 1998). The storage coefficient of

151 MU-104 at *c.a.* 1000 m in the infra-molassic sands is only 1.5×10^{-4} thus confirming the confined
152 character of the aquifer. The transmissivity ($1.8 \times 10^{-5} \text{m}^2 \cdot \text{s}^{-1}$) and the estimated permeability (
153 $1.0 \times 10^{-6} \text{m} \cdot \text{s}^{-1}$) are low too for MU-104 borehole. The yield rate of PO-101 was not evaluated by
154 pumping during its conversion into a piezometer but by the means of swabbing that again suggested
155 a low productivity (AFBAG, 1974). The two shallower boreholes (LBG and VLD) have storage
156 coefficients of 1.0×10^{-2} , suggesting that the confined character exists even close to the recharge
157 area. The productivity is also low (transmissivities of $6.5 \times 10^{-5} \text{m}^2 \cdot \text{s}^{-1}$ for LBG and $5.0 \times 10^{-5} \text{m}^2 \cdot \text{s}^{-1}$
158 for VLD).

159 As for hydraulic properties, only little information is available on water quality at depth and most of
160 the available data are for equipped boreholes. Deep sampling in such boreholes is publicly reported
161 only once, together with physico-chemical characterization of the water column, but far above the
162 perforations (Négrel *et al.*, 2008).

163

164 **3. Methods**

165 **3.1 Borehole characterization**

166 Because the integrity of old boreholes is poorly constrained, endoscopic (camera) inspections were
167 completed in some boreholes (LC-101 and PO-101) prior to any other investigation, in order to check
168 borehole integrity. This diagnostic has not been done in the shallower boreholes (LBG and VLD),
169 because they benefit from better knowledge. Physico-chemical logging has been done in LBG and
170 VLD (by BRGM) and in LC-101 and PO-101 (by a subcontractor, Hydro-Assistance). Physico-chemical
171 logging has been done first under natural flow conditions and, if possible, during and/or after
172 pumping, in order to help in locating the water inflows in the boreholes. Probes used were Idronaut
173 303 or 316 models equipped with pressure, temperature, electrical conductivity, pH, redox and
174 dissolved oxygen sensors. No endoscopic or physico-chemical logging were done in MU-104.

175

176 **3.2 Pumping**

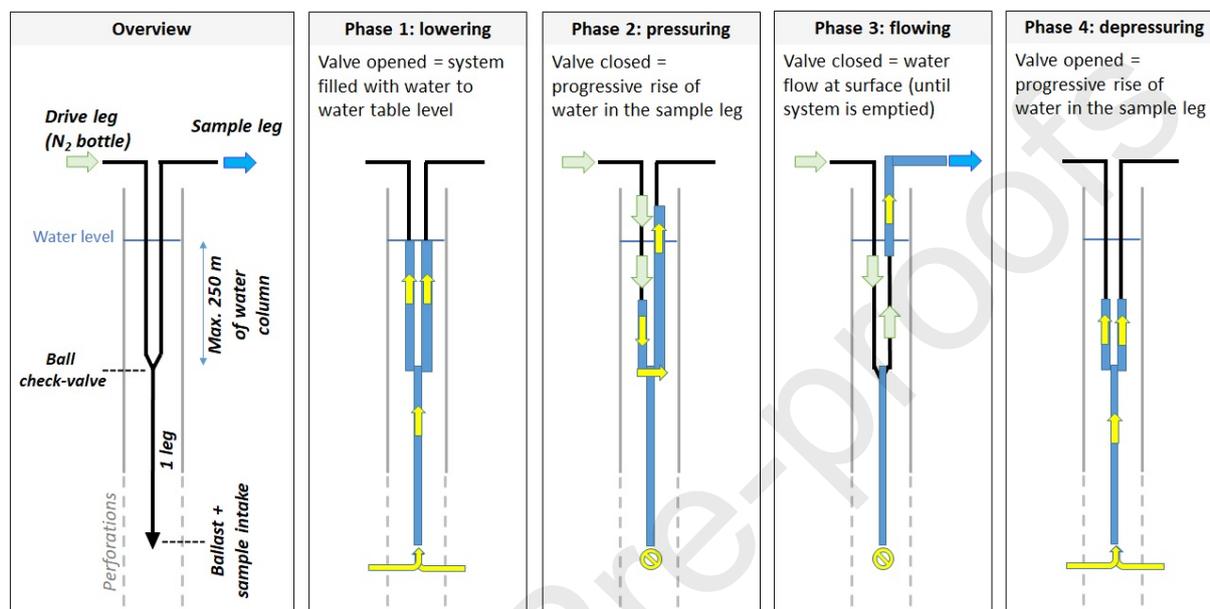
177 The strategy of pumping also differed from boreholes to others. There was no pumping in MU-104.
178 Sequential pumping was performed in the shallow boreholes (LBG and VLD) using a 2 inches pump
179 (max. flow rate $<2 \text{ m}^3 \cdot \text{h}^{-1}$). A larger pump (4 inches) was used by the subcontractor to produce water
180 from PO-101 (flow rate: $4.3 \text{ m}^3 \cdot \text{h}^{-1}$) and LC-101 (flow rate: $4 \text{ m}^3 \cdot \text{h}^{-1}$).

181

182 **3.3 Deep sampling**

183 Deep sampling was performed using the BRGM GOG (for Gaz-O-Gaz) proprietary system (Gal *et al.*,
184 2014, 2017). Like the U-tube system (Freifeld *et al.*, 2005), the GOG sampling system is based on the
185 use of ball check-valve operated by pressure of a neutral gas (nitrogen). The gas pressure is applied
186 to the drive leg, and the sample is collected from a second leg, the sample leg (Figure 2). Unlike the
187 U-tube system, the GOG system is a mobile and retrievable system, made of flexible tubing
188 (polyamide), which can be lowered to any depth in a borehole. If the system is operated several
189 times in a borehole, logging-like information can be obtained. This allows *e.g.* performing several
190 sampling in a perforated horizon. In order to optimize the efficiency of valve functioning and to
191 operate with reasonable gas pressure, the ball check-valve is deployed under 250 m of water column
192 at maximum. The nitrogen pressure to apply to get water flowing at the surface is thus 25 bars plus
193 some additional bars linked to pressure losses, in the range of admissible pressure of the flexible pipe
194 (working pressure 25 bars; burst pressure 50 bars). Below the ball check-valve, a unique leg, with a
195 ballast, is deployed down to the desired sampling depth. It acts as a straw: when deployed, it fills
196 with water from the entire water column. A purging phase is thus needed to get water from the
197 horizon to be sampled. In case of little depth changes from one location in the borehole to the other,
198 the geometry of the GOG system is fixed and defined prior the investigations (Figure 2). In case of
199 large interval between the sampling depths (MU-104), the system is retrieved at the surface, and its
200 geometry adapted, between each use of the system. By geometry, the GOG system has an internal

201 capacity of 1.25 L per 100 m of leg deployed under the water level. The total volume of water is thus
 202 2.5 L per 100 m between the valve and the water level. The duration of a cycle, *i.e.* the time between
 203 the end of one water flow and the following one, is 15 minutes; Figure 2 describes the working
 204 principle of the GOG system.



205
 206 Figure 2: principle of sampling using the GOG system: from left to right: generic scheme of a GOG
 207 deployment in a borehole; working principle in four steps: 1: lowering of the system in the borehole
 208 (valve open); 2: nitrogen pressuring (closing of the valve and initiation of fluid ascent in the sample
 209 leg); 3: fluid production from the sample leg until the drive and sample legs are emptied; 4: valve
 210 opening by pressure release (initiation of water ascent in the drive and sample legs, from the leg
 211 deployed below the valve; after completion, the system is in step 1 configuration).

212

213 **3.4 Laboratory analyses**

214 Major elements were analysed for LBG, VLD, LC-101, MU-104 and PO-101. Trace elements were
 215 analysed for LBG, VLD, LC-101 and PO-101. Samples were filtrated (0.45 μm) on site and acidified
 216 when required.

217 Isotopes of the water molecule ($\delta^{18}\text{O}$ and δD) and isotope of the sulfates ($\delta^{18}\text{O}_{\text{SO}_4}$ and $\delta^{34}\text{S}_{\text{SO}_4}$) were
218 determined for MU-104 and PO-101 (the characterization of LC-101 samples is not discussed here).
219 Other isotope characterizations were done for LC-101 and PO-101 and are discussed by Barrière *et al.*
220 (2019).

221

222 **4. Results**

223 **4.1 Endoscopic inspection**

224 Prior characterizing groundwater using depth specific sampling, it is important to get as many
225 information as possible about the well completion. In that perspective, endoscopic inspections were
226 performed in LC-101 and PO-101. Camera investigations were stopped prematurely in LC-101
227 because an oil supernatant was observed above the water table. A skimming pumping of 4 m³ had
228 therefore to be done.

229 The PO-101 borehole has been investigated down to the perforated horizon. The video record
230 showed a casing in relatively good conditions, with minor oxidation above the water level. Some
231 scalings are visible above the perforated section and over the perforations (818-829 m). The
232 borehole is obstructed at 951 m, possibly by sediments from the above perforations.

233

234 **4.2 Pumping and physico-chemical logging**

235 Because it is important to assess if deep boreholes can be used for deep sampling and subsequent
236 chemical characterization, whatever their use, some of them were investigated more in details in
237 order to better understand their own dynamics. These investigations were done in two-steps. Step-1
238 characterizations enclose well logging at equilibrium conditions and deep sampling, then followed by
239 pumping and a second deep sampling session at the levels previously monitored. This approach was
240 used first in the shallow boreholes LBG and VLD, in order to define the best approach, and then at
241 PO-101. For Step-2 characterizations, deep sampling is only performed after pumping (LC-101). This

242 approach was not used at MU-104, where deep sampling was performed without any preliminary
243 characterization.

244

245 **4.2.1 Boreholes characterized before and after pumping – shallow wells**

246 The results of physico-chemical logging of the shallow LBG and VLD boreholes are given in Figure 3.
247 Only one logging operation was previously reported in LBG borehole (Négrel *et al.*, 2006), but only
248 down to 100 m bgl., *i.e.* in the cased section, so that no information exist on the physico-chemical
249 evolution in the screened section.

250 Albeit the LBG and VLD boreholes are shallow, they have a specific response to pumping, directly
251 linked to their transmissivities. The LBG borehole cannot be pumped at high flow-rate. During the
252 investigations, the maximum flow-rate was $1.1 \text{ m}^3 \cdot \text{h}^{-1}$ and it induced a drawdown of 19 m in 3 hours.
253 The pumping had then to be stopped to prevent dewatering of the submersible pump. The water
254 level recovery after pumping is slow, with +9 m in 3 hours. The VLD borehole was pumped at a
255 slightly higher flow-rate ($2 \text{ m}^3 \cdot \text{h}^{-1}$) and the maximum drawdown was 8 m in 4 hours. The rise in water
256 level after pumping is faster, with +6 m in 15 minutes.

257 As earlier mentioned, the LBG and VLD boreholes were logged several times prior, during and after
258 pumping. For each borehole, the pumping was operated over 3 days, with periods of rest. In LBG, 7.3
259 m^3 were abstracted in 8.5 hours, representing 1.6 times the volume of the water column. In VLD,
260 14.6 m^3 were abstracted in 9 hours, representing 3.5 times the volume of the water column. These
261 values are in line with those recommended for getting a representative sample (*e.g.* US-EPA, 1999)
262 but they were reached over a 3-days period, which underlines the very low productivity of VLD and
263 especially LBG boreholes. As these boreholes are punctually surveyed for water quality purposes, a
264 better understanding on the way they behave is thus important.

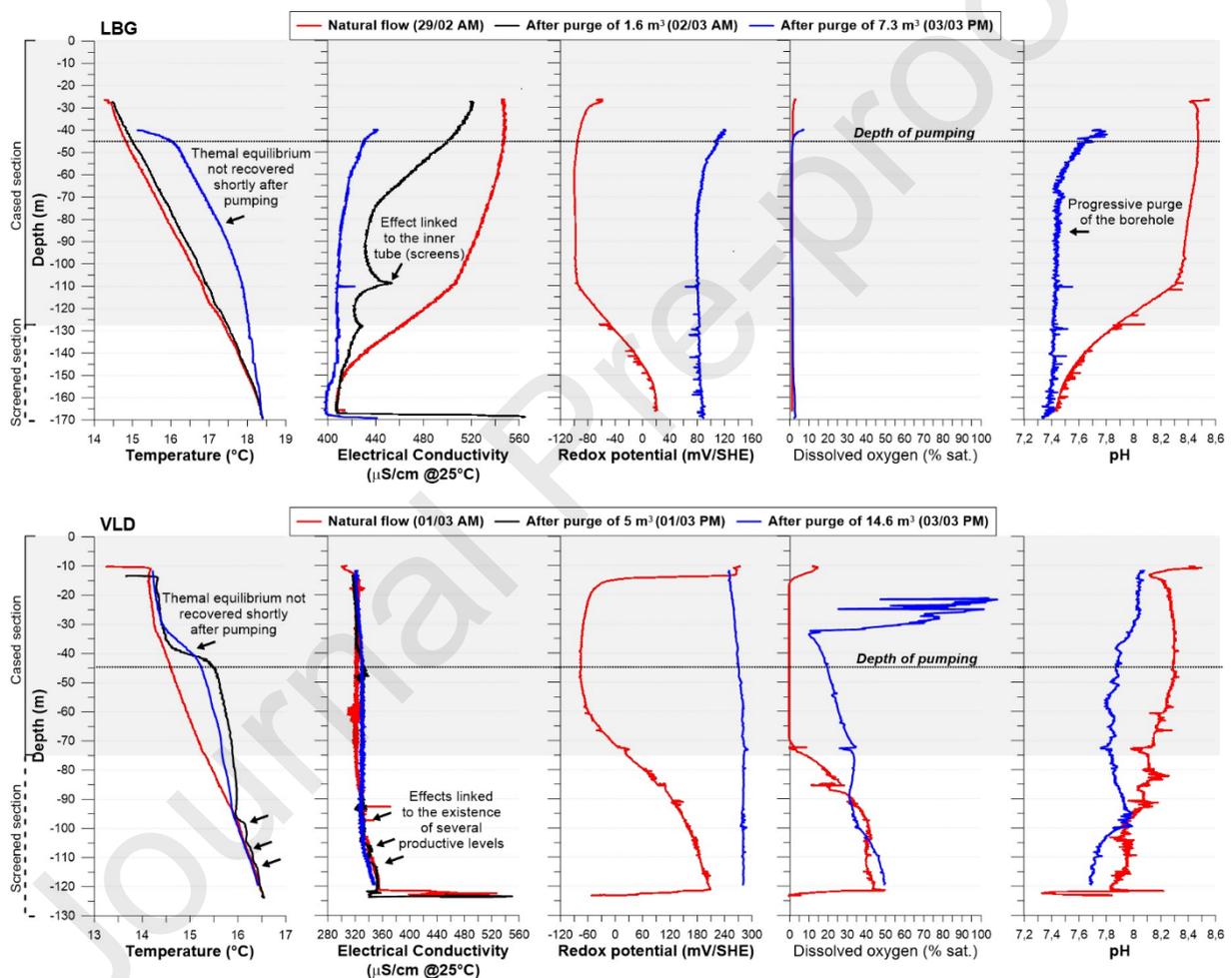
265 Under natural flow conditions (Figure 3), LBG had a linear temperature profile with an increase of
266 $2.97^\circ\text{C}/100 \text{ m}$, very close to the mean geothermal gradient. No thermal gradient could be seen from

267 10 to 30 m below ground level in VLD and the measured gradient under 30 m was lower than at LBG
268 with a mean value of 2.44°C/100 m. This may be related to different ground conditions, the existence
269 of shallower aquifers, which modifies the local gradient at VLD. The pH and redox evolution of LBG
270 and VLD were similar, with pH values higher and redox values lower in the cased section, probably
271 because of interaction with steel. The shape of electrical conductivity curves was different: there was
272 no change between the cased section and the screened section in VLD, whereas the electrical
273 conductivity was higher in the cased section of LBG. Again, for LBG, this argues for interaction with
274 the casing. For VLD, it may suggest the existence of well-bore flow as may be postulated with the
275 temperature log. Both dissolved oxygen values were close to zero in the cased section and this
276 remained only valid in the screened section for LBG. For VLD, there was some remaining dissolved
277 oxygen in the aquifer. The fact that oxygen did not exist in the cased section of VLD does not argue
278 for well-bore flow.

279 The shape of the profiles evolved when the boreholes were pumped sequentially (Figure 3). The
280 progressive renewal of water in the cased section was particularly well illustrated for LBG. The
281 electrical conductivity, pH and redox profiles became vertical from bottom to top, further suggesting
282 that the water inflow was mostly originated from the bottom part of the screened section (the last
283 20 m). . From the electrical conductivity profile, it may be inferred that the renewal of 1.6 times the
284 volume of the water column (7.3 m³) is the lowest admissible limit for column renewal because the
285 conductivity at 45 m depth is still 5% higher than the conductivity at 150-170 m depth. Any lower
286 abstracted volume may lead to erroneous characterization of the aquifer water, as shown by the
287 conductivity profile obtained after the purge of 1.6 m³ (*i.e.* after 1.5 hours of pumping). This is a
288 demonstration of the need to purge boreholes even if they have low water production when
289 sampling is done by pumping.

290 This pumping phase is less critical for VLD borehole. Indeed, the electrical conductivity profile was
291 already vertical prior to pumping, and the situation remains the same when pumping. The pH, redox

292 and dissolved oxygen profiles did also verticalize albeit there was a rise of the oxygen data in the
 293 upper section of the casing probably related to air intrusion in the borehole. The location of the
 294 water inflow was again in the lower part of the cased section. A closer look to the conductivity profile
 295 and especially the temperature profile infers that the thermal profile was a step profile, horizons of
 296 stable temperature alternating with horizons of steep gradient as indicated by the arrows on Figure
 297 3. Horizons characterized by temperature step gradient are logically productive levels, suggesting
 298 that water inflow in VLD is the result of the mixing of several productive levels (at least 3).



299

300 Figure 3: physico-chemical logging of LBG and VLD boreholes. Log under natural flow in red, log after
 301 pumping in blue. An intermediate logging step is plotted in black.

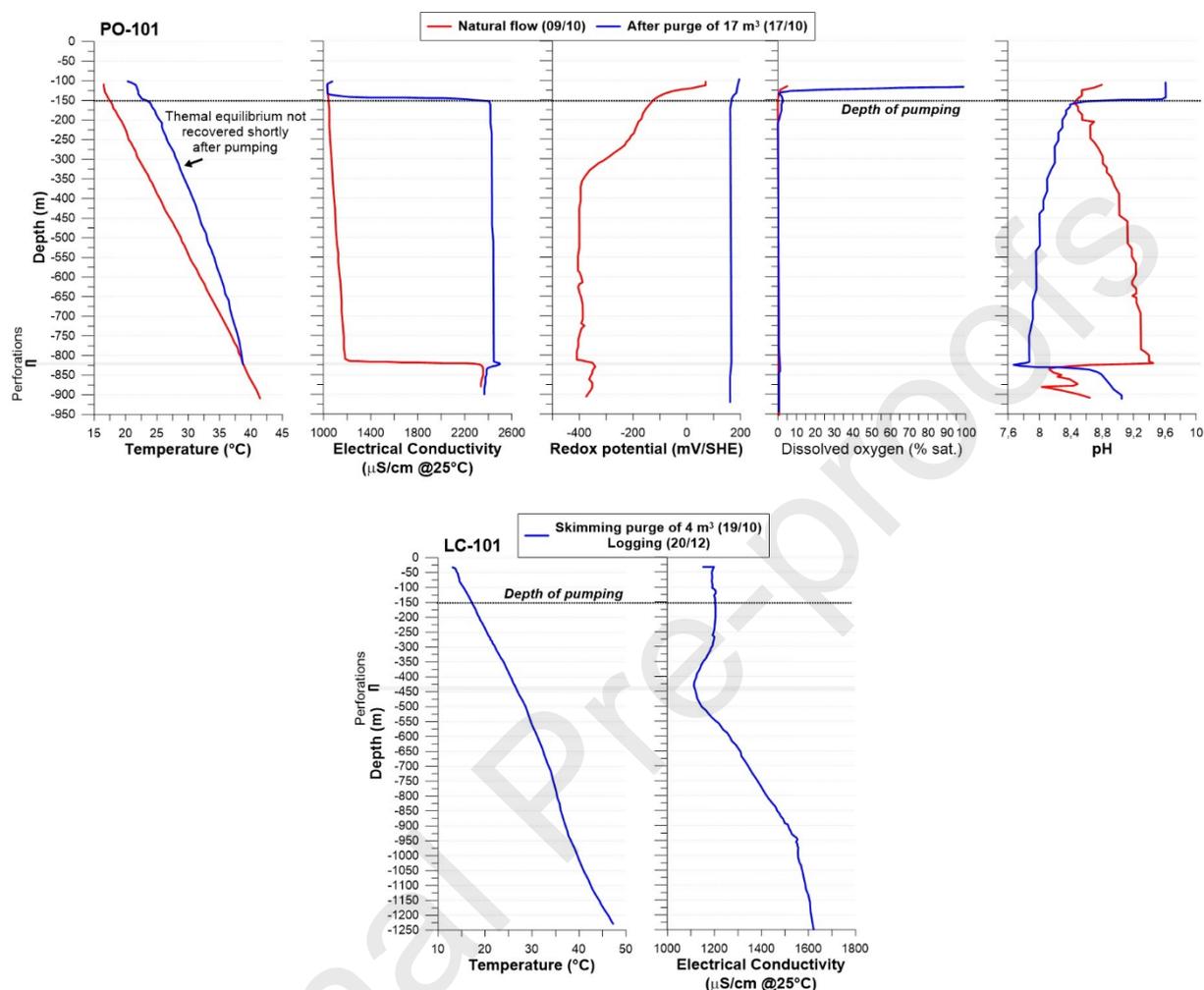
302

303 4.2.2 Boreholes characterized before and after pumping – deep wells

304 The results of physico-chemical logging of the deep PO-101 borehole are given in Figure 4. Under
305 natural conditions, PO-101 showed a nearly vertical profile of the electrical conductivity down to 780
306 m depth with values slightly increasing from 1020 to 1170 $\mu\text{S}\cdot\text{cm}^{-1}$ (at 25°C). Correlatively the pH
307 increased from 8.6 to 9.4. The redox potential was reducing, in accordance with the absence of
308 dissolved oxygen. Such profiles characterize the interaction of a stagnant water with the steel casing.
309 These profiles argue for the absence of casing failure as already suggested by the video inspection.
310 Additionally, there is no developed upward migration of water from the bottom to the surface. The
311 thermal gradient is linear, demonstrating that there is no influence of water migration outside the
312 casing. This gradient is consistent with the mean geothermal gradient (3.2°C/100 m). The physico-
313 chemical logging demonstrates that the water inflow is originated from horizons below 780 m depth,
314 likely from the perforated interval. This water inflow is particularly noticeable on the electrical
315 conductivity data (Figure 4). Within a few meters (from 815 to 828 m), the value of the electrical
316 conductivity doubles to reach 2300 to 2400 $\mu\text{S}\cdot\text{cm}^{-1}$. In the meantime, the value of the pH decreases
317 to 8.2. The temperature gradient is also locally perturbed in the 780 – 840 m depth interval,
318 suggesting that some water circulates outside the casing between the Ypresian formation, the base
319 of which is tapped by the perforations, and the underlying Paleocene aquifer and/or the overlying
320 Lutetian formations.

321 Based on this log, it may be inferred that deep sampling performed without any borehole stimulation
322 can bring water representative of the formation water in PO-101. The log performed after pumping
323 corroborates this observation. A volume (17.2 m³) slightly greater than that of the water column
324 between the pump (set at 150 m depth) and the perforations (16.5 m³) was abstracted in 4 hours
325 (Figures 1 and 4). After pumping, the water column is entirely renewed as indicated by vertical
326 electrical conductivity, pH and redox logs. The temperature log is modified by the action of pumping
327 as warmer water is progressively drained from depth to the pump intake. All these data point to the
328 absence of water inflows above the perforated interval. Below this interval, the physico-chemical

329 parameters are not modified, indicating that the bottom-hole is not productive. The perforated
 330 interval is thus the only water provider in PO-101 borehole.



331
 332 Figure 4: physico-chemical logging of PO-101 and LC-101 boreholes. Log under natural flow in red, log
 333 after pumping in blue.

334

335 4.2.3 Boreholes characterized only after pumping

336 The LC-101 borehole was purged to skim the oil supernatant and no physico-chemical logging could
 337 be done before this action. The water column was logged with a rugged device equipped with only
 338 temperature and conductivity sensors two months after the skimming purge.

339 Figure 4 shows the result of this logging. The temperature profile is similar to a natural profile,
340 without pumping because the temperature gradient between the static level and 600 m depth is
341 linear (+3.2°C/100 m). Between 600 and 900 m depth, the gradient is lower (+1.9°C/100 m) and it
342 goes back to geothermal gradient below (+3.1°C/100 m from 900 to 1200 m depth). This suggests
343 that some water movement exists outside casing between 600 and 900 m, but the perforated
344 interval is supposed to be well above (430-440 m; Figure 1). At this perforated level, the electrical
345 conductivity profile reached its lowest value (close to 1100 $\mu\text{S}\cdot\text{cm}^{-1}$; Figure 4). This was likely a
346 consequence of a water inflow, which penetrates the borehole at the perforations' level. The
347 conductivity profile above 430 m was smoothed compared to profiles obtained shortly after
348 borehole purging (Figure 4) because of diffusive processes inducing the occurrence of a chemical
349 gradient between low mineralized waters (from the perforations) and more mineralized waters (in
350 the cased section). Below 440 m, the conductivity progressively increased up to 1600 $\mu\text{S}\cdot\text{cm}^{-1}$ around
351 900 m depth, depth from where the conductivity value varies little. Such a profile does not argue for
352 the existence of other inflows at depth.

353

354 **4.3 Water chemistry**

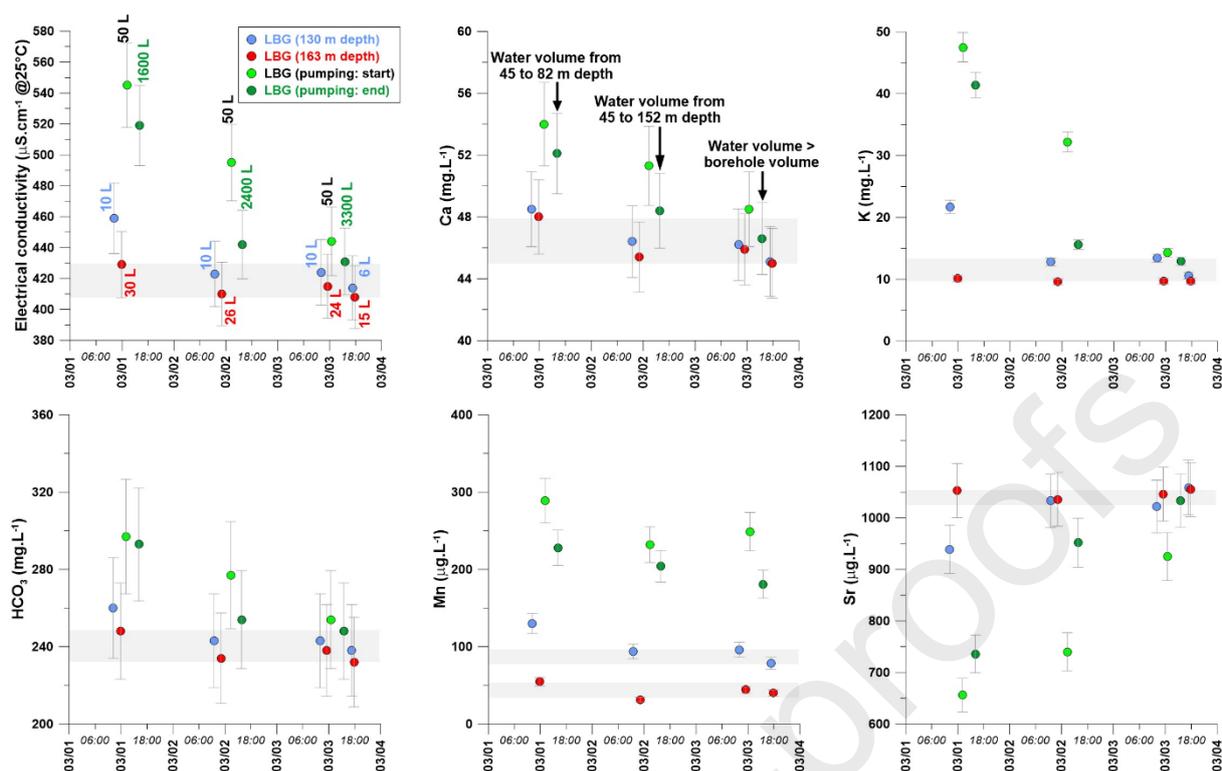
355 Major elements and trace elements analyses are given in supplementary information for depth
356 discrete samples and for samples obtained by pumping (LBG and VLD boreholes). Chemical balance
357 of the analyses is between -3% and +1%.

358 **4.3.1 Quality of the depth specific samples**

359 An assessment of the representativeness of the samples acquired during the deep sampling
360 operations, and therefore a way to get a quality control on these depth specific samples, is given in
361 Figure 6. This figure compares, for the LBG borehole and for some parameters and dissolved
362 elements concentrations, the results obtained using the GOG system and the results obtained using
363 the classical pumping approach (pump set at 45 m depth; Figure 1). The first two discrete samples at

364 130 and 163 m depth were taken without any wellbore purging with a circulation of respectively 10 L
365 and 30 L of water in the system prior to sampling. The electrical conductivity therefore represents
366 the conductivity existing at 130 and 160 m depth under natural flow conditions (Figure 3). When
367 some wellbore purging is done, the water column homogenizes in the screened section and
368 subsequent depth specific samples have minor variability in conductivity and dissolved elements
369 (Figure 5). Depth specific samples are thus representative of the chemistry of their respective depths
370 at the time they were taken. In the present case, this may suggest that the 130 m depth horizon has
371 a higher conductivity and is slightly more enriched in K than the 160 m depth horizon. These
372 differences disappear after the first purge of 1.6 m³ confirming that the 130 m depth horizon is not
373 representative of most of the water from the aquifer. Secondly, there is minor variability of the
374 depth discrete samples taken when some water is abstracted from the borehole, indicating that
375 there is no contamination by the sampling system. This is illustrated by the major and trace
376 concentrations measured at 160 m depth, which are invariant for all the samples whatever their time
377 of collection, before or after purging.

378 As expected, the representativeness of samples obtained by pumping is much longer to obtain. The
379 abstraction of large volumes of water is required first to purge the volume of water between the
380 pump and the top of the screens in the cased section. This purge operates like the movement of a
381 piston, with renewed water gradually moving upward from the screened section to the cased
382 section. Consequently, the purge of more than 4 m³ is required to get water samples that have a
383 similar composition than that obtained by discrete sampling at depth (Figure 5). For some trace
384 elements, even the purge of more than one water column volume is not sufficient to achieve
385 representativeness, as illustrated by Sr and especially Mn concentrations. For these two elements,
386 depth discrete sampling gives more precise information, perhaps indicating the existence of some
387 heterogeneities in the aquifer to which pumping actions are blind.



388
 389 Figure 5: comparison of electrical conductivity, Ca, K, HCO₃, Mn and Sr concentrations acquired
 390 during discrete sampling and during pumping (LBG borehole). The volumes reported for depth
 391 specific samples correspond to the volume of water purged at the depth of sampling prior sampling
 392 action. The volumes reported for pumping correspond to sampling shortly after pump start and to
 393 sampling after some m³ were purged. The grey fields show the variability of the data for the depth
 394 specific samples (the first sample taken at 130 m depth is excluded – see text for explanations).

395 396 4.3.2 Water chemistry

397 There is a clear connection between the depth of the screened section or the perforated interval and
 398 the mineralization of the fluid (Supplementary information). The shallowest borehole (VLD) has the
 399 lowest mineralization (Total Dissolved Solids equivalent to 280 mg.L⁻¹) and the deepest one (MU-104)
 400 the highest (TDS of 2920 mg.L⁻¹). Two groups can be identified: low concentrated waters (TDS < 420
 401 mg.L⁻¹), with dominant Ca-Mg and HCO₃, and more mineralized waters (TDS > 630 mg.L⁻¹), with
 402 dominant Ca and Cl-SO₄. Only the VLD samples have measurable, but low, NO₃ amounts, indicating
 403 that nitrate has not been completely reduced. This is in agreement with the slightly oxidant character

404 of the water. The overall trend is an increase in mineralization with depth, which is a classical trend in
405 groundwaters in large sedimentary basins, mineralization being generally associated to longer
406 residence time and more interaction with the aquifer matrix.

407 Also, a connection can be seen between the depth of the water inflow and the content in trace
408 elements and especially elements sensitive to water-rock interaction processes. The content in Sr
409 increases from $770 \mu\text{g.L}^{-1}$ at VLD to 3700mg.L^{-1} at MU-104. Salinity indicators such as B or Br (when
410 measured) follow the same trend. Conversely, higher concentrations in Li can be seen in LBG, greater
411 than in MU-104 (306 and $234 \mu\text{g.L}^{-1}$ respectively), suggesting an interaction with Li-rich rock matrix in
412 relatively shallow environment.

413

414 **4.4 Isotopes**

415 Some isotope measurements were done on the samples collected in the deep boreholes
416 (Supplementary information). Sulfur and oxygen isotopes of the dissolved sulfates and hydrogen and
417 oxygen isotopes of the water molecule were analyzed for MU-104 and PO-101. Sampling was
418 performed before and after pumping in PO-101 in order to determine if some variations occur when
419 the borehole is partially purged. The values are the same before and after pumping, suggesting that
420 direct deep sampling at the perforated depths can provide representative information at least for
421 these isotopes.

422 The samples performed at several depths in MU-104 provide further information about
423 representativeness along the water column, especially at depths far from the perforated interval.
424 There is almost no change along the water column for oxygen and hydrogen isotopes of the water
425 molecule considering the uncertainty on the measurement. At the opposite, there is significant
426 variation for the sulfates, especially for the sulfur isotopes and to a lesser extent for the oxygen
427 isotopes. When the sampling is performed at the level of the perforations (1035 m), the volume of

428 water purged during deep sampling seems to have no influence on the result and this result probably
429 reflects the real value of sulfur isotopes in the aquifer.

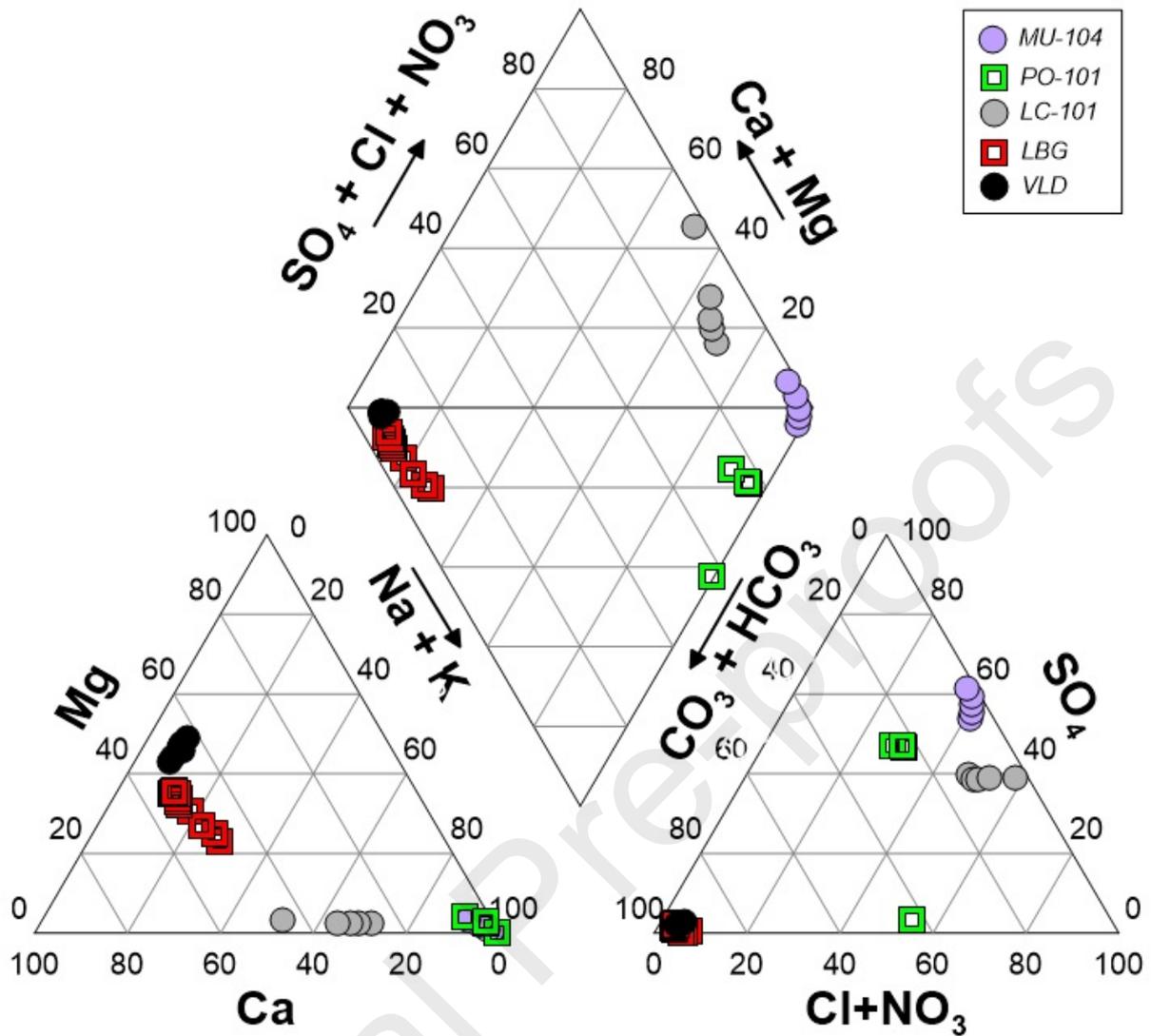
430

431 **5. Discussion**

432 ***5.1 Certainties and uncertainties in the characterization of the Paleocene – Eocene aquifer***

433 The goal is not to get an in-depth description of the water-rock interactions processes but rather to
434 determine to what extent the new acquired data can be included in existing databases and if they
435 put light on new findings.

436 Data from VLD borehole match the ideal expectations for the functioning of a borehole (Figure 6;
437 Supplementary information). There is minor difference from one sample to the other whatever the
438 monitoring approach and the depth of sampling. The data are in good agreement with those
439 reported just after the borehole was completed (BSS EAU, 2020b). Provided the sampling material is
440 in good condition and some water renewal is allowed prior to sampling, investigations in such a
441 borehole are likely to bring representative samples when using a pump. A similar observation can be
442 made if the water is sampled using a deep sampling system provided it is deployed in the screened
443 interval. The best fit between deep sampling and pumping is obtained after one purging session (one
444 water column volume), suggesting that some enhanced water production may be needed to renew
445 the water column at depth.



446
447 Figure 6: Piper diagram of all the waters sampled in the Paleocene-Eocene aquifer (depth discrete
448 samples and samples by pumping).

449

450 Albeit being located close to VLD, the LBG borehole has a more complex functioning as illustrated by
451 Figures 5 and 6 (and Supplementary information). Contrary to what is observed for VLD, all the new
452 data differ from the data reported shortly after borehole completion in 1990 (BSS EAU, 2020c) and
453 from the data reported by Brenot *et al.* (2015). The data acquired after completion may be
454 unrepresentative of the chemistry of the aquifer if the borehole development has not been fully
455 achieved in relation with the low water production. The water analysis reported in 2015 is
456 surprisingly enriched in Cl and SO₄ and depleted in Mg and no obvious explanation can be suggested.

457 This sample was taken in 2006 (Négre *et al.*, 2006), and at this time borehole logging was done only
458 down to 100 m below ground level, so the complete renewal of the water column could not be
459 checked. If the pumping was too short to renew the whole water column, then part of the
460 discrepancy may be related to changes in water chemistry resulting from interactions with the
461 casing. Indeed, a similar enrichment in K or Cl was measured in the first sample taken while in the
462 LBG borehole (Figure 5), but no Mg depletion or SO₄ enrichments can be seen. While purging, the
463 water chemistry progressively shifts to more and more reproducible values.

464 The comparison with deep sampling is informative as such. Some differences can be seen between
465 the first two downhole samples at 130 and 163 m depth, and only the last one appears to be
466 representative of the chemistry obtained at the end of well pumping (Figure 5). This confirms that
467 the water inflow in LBG borehole occurs mostly from the bottom of the screened interval, as earlier
468 demonstrated by physico-chemical logging. As the purge increases, the water at 130 m depth is
469 progressively renewed by the upward flow, leading to a convergence of chemical data at the end of
470 the sampling session. At that time, all the water in the screened interval has been completely
471 renewed and even higher up to the pump intake.

472 As a consequence, downhole sampling, if performed in the screened interval and where water flows
473 in, can bring interpretable data even if performed without preliminary water abstraction.

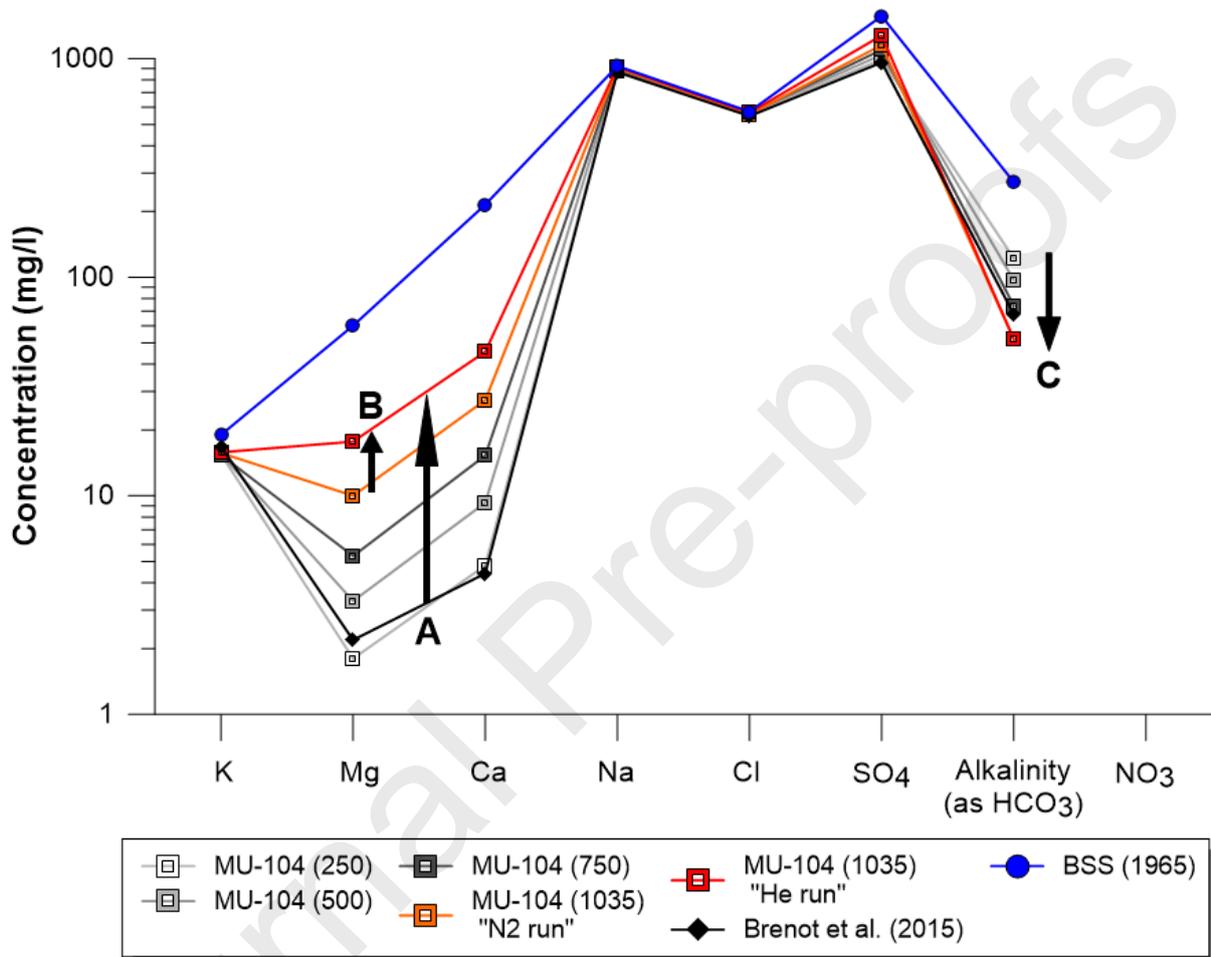
474 Nevertheless, some pumping actions may be operated as a quality insurance approach, in order to
475 ensure that some water production has occurred at depth.

476 A good representativeness of water samples can thus be obtained when the deep sampling system is
477 driven in the appropriate sections of boreholes. Conversely, sampling in inappropriate depth leads to
478 erroneous characterizations, as demonstrated in Figure 7 with MU-104 samples. The first sampling,
479 done at 250 m depth, has a chemical composition similar to that of the analysis reported by Brenot
480 *et al.* (2015) at a similar depth. If this demonstrates some reproducibility in the sampling actions over
481 years, this does not mean that this 250 m depth sample is representative of the chemistry of the

482 Eocene aquifer. This is clearly illustrated by the chemical composition of deeper samples (500, 750
483 and 1035 m). There is a progressive enrichment, along the casing, in Mg and Ca, and to a lesser
484 extent in SO_4 (path A in Figure 7), and conversely a progressive depletion in alkalinity and a pH
485 decrease (Supplementary material). The same pattern can be observed in time while increasing the
486 volume of water abstracted using the GOG system at the perforations depth (path B in Figure 7),
487 without reaching the 1965 data, obtained when the borehole was converted into a piezometer. This
488 1965 sample reveals a high mineralization of the water (about 3.6 g/L), clearly higher than the water
489 sampled in the same geologic formation in neighbor wells (about 0.5 g/L - Vandenberghe, 1966).
490 According to the author, the sample is not representative of the formation water because of the
491 many cleaning operations after perforating. High amounts of hydrochloric acid (HCl) and ammonium
492 hydrogen fluoride ($\text{F}_2\text{H NH}_4$) acid were injected in 1965 and only half of these amounts were pumped
493 back. The consequence was the measurement of high concentrations of chloride (572 mg/L) and
494 fluoride (17 mg/L) which are still observable today at the bottom of the well. Assuming that the 1965
495 data were not representative of the aquifer chemistry at the time of collection, then the new data
496 confirm that the contamination (by chloride and fluoride) is still present 50 years later. This reveals
497 an insufficient water renewal at depth through the perforations and a too low purged volume (about
498 60 liters) from the 1035 m depth.

499 Nevertheless, even if the representativeness of the 1035 m depth samples may be questioned, the
500 behavior of dissolved species at 1035 m and in the water column can be discussed. First, the Ca
501 content at 1035 m depth is consistent with a water in equilibrium at 45°C with calcite and a pCO_2
502 close to $10^{-3.5}$ atm (according to calculations with PHREEQC code – Parkhurst and Appelo, 2013).
503 Then, the alkalinity increase in the cased section (path C in Figure 7) is probably due to two chemical
504 processes occurring in the water column: *i*) corrosion of the casing, involving a pH increase and a
505 decrease of Mg, Ca and Mn concentrations (Nilsson and Sandberg, 2017); and *ii*) sulfate reduction by
506 micro-organisms as revealed by sulfate isotopes (see following paragraph). The sulfate reduction
507 involves the production of sulfides (about 1 mmol/L under HS^- form because of pH conditions)

508 increasing the alkalinity of waters and the decrease of their redox potential. The sulfate reduction
 509 seems to be the main process impacting sulfate since the precipitation of SO_4 -rich phases (anhydrite,
 510 gypsum) is not supported by calculation of saturation indexes, which are always negative and thus
 511 not indicating developed precipitation.



512

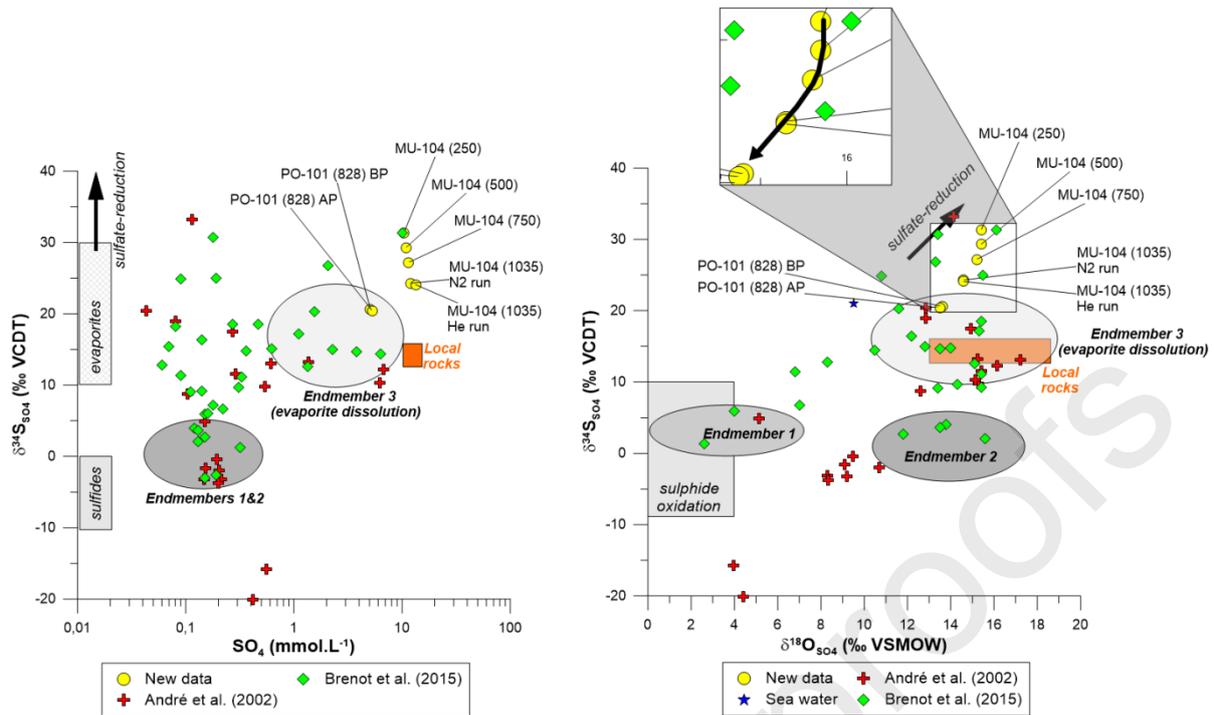
513 Figure 7: Schoeller diagram for MU-104 samples; note that the alkalinity is expressed as the HCO_3
 514 content; some contributing species may not have been quantified.

515

516 Another process can decrease the concentration in sulfate. Figure 8 reports the evolution of S and O
 517 isotopes of the SO_4 for MU-104 and PO-101. There is no change of isotope signature for PO-101
 518 when comparing samples acquired before and after water abstraction by pumping. This suggests that
 519 water flow through perforations at depth is sufficiently developed in PO-101 and that representative

520 samples can be obtained after a minor purge. The two samples obtained at 1035 m in MU-104 also
521 have very comparable isotope values albeit their concentrations in SO_4 are slightly different. When
522 including the samples obtained in the cased section, the S-isotope ratios still point to an origin of the
523 sulfates related to interactions with evaporitic formations, as earlier reported by André *et al.* (2002)
524 and Brenot *et al.* (2015). But their plot with the O-isotope values of the SO_4 (black arrow in the right
525 inset of Figure 8) leans from high ratios to lower ones, as a function of depth. The information
526 obtained at the level of the perforations is very close to the endmember representing the interaction
527 with local evaporites. In their 2015 paper, Brenot *et al.* reported a value obtained with a sampling at
528 250 m and they suggested that such a sampling may not be representative. This non-
529 representativeness is clearly established here with the new results. There is no need to refer to
530 mixing between endmembers to attribute the origin of sulfates in MU-104. This origin is the same as
531 for many other boreholes tapping the Eocene aquifer but, depending on the sampling depth, sulfate-
532 reduction processes occur in the casing and strongly alter the isotope signature of the sulfates.

533



534

535 Figure 8: left: $\text{SO}_4 - \delta^{34}\text{S}_{\text{SO}_4}$ relation; right: $\delta^{18}\text{O}_{\text{SO}_4} - \delta^{34}\text{S}_{\text{SO}_4}$ relation. Endmembers 1, 2, 3, and local
 536 rock fields as defined by Brenot et al. (2015).

537

538 It is interesting to mention that not all the isotope ratios are modified by a long contact period with
 539 steel casing. An example can be found in Supplementary information with the oxygen and hydrogen
 540 isotopes of the water molecule. All the samples collected in the water column of MU-104 point to
 541 the same isotope value, minor variation being linked to the uncertainty on the measurement. The
 542 data obtained at 250 m depth give thus reliable indication on the recharge processes experienced by
 543 the MU-104 waters. The samples from PO-101 follow the same rule, with minor variations when
 544 sampled before or after borehole pumping.

545

546 **5.2 Learnings from borehole characterization and deep sampling**

547 The first outcome is for relatively shallow boreholes (LBG and VLD – tapped sections located from
 548 around 100 to 160 m bgl). In such boreholes, downhole sampling can be performed with a high level

549 of confidence provided the completion of the borehole is known and the levels of water flow in the
550 screened interval are located. In the absence of good knowledge of waters flows and the evolution of
551 the borehole equipment, some water abstraction may be required to ensure water renewal in the
552 screened section.

553 The second outcome is for deep boreholes and it splits into several subgroups. When the water flow
554 is supposed to be not too low, as in PO-101, deep sampling can be operated without water
555 abstraction. The situation becomes then similar to that of shallow boreholes. Because knowing if
556 water flows are not too low, if the screens are not scaled or if the completion is not damaged is often
557 tricky, complementary actions may be required before sampling downhole to ensure of
558 representativeness of the sampling action. The first is to perform water abstraction to ensure some
559 water renewal. This may provide information on continued existence of connectivity with the aquifer
560 by following the water level over time but this does not provide information on the levels from which
561 water is produced. This information can be obtained by flow logging in a borehole but also from deep
562 sampling operations. Deep sampling performed in the perforations/screens prior to pumping and
563 repeated when the pumping is active, with potentially displacement of the sample intake of the
564 system, helps to locate where there is some water renewal at depth and therefore where there is
565 connectivity to the aquifer. Because these operations may be time consuming, the use of alternative
566 information sources, such as water logging and/or video inspection, may be preferred, but, in turn,
567 such investigations may become costly. As a result, there is often a lack of knowledge of the
568 functioning of deep boreholes, which is regrettable from a representativeness point of view. This
569 may result in biased understanding of the aquifer chemical properties and reporting of non-
570 representative data.

571 In spite of this lack of characterization of the water flows in deep boreholes, the present study has
572 demonstrated that the combined used of deep sampling techniques and preliminary abstraction of a

573 water volume equivalent to that of the screened section/perforated interval may be sufficient to get
574 realistic description of the water-mass.

575

576 **6. Conclusions**

577 Deep sampling techniques were used to characterize the Eocene aquifer in the Aquitaine basin. The
578 observed boreholes ranged from 130 to more than 1000 m in depth thus excluding, or making the
579 use of a pump complex and costly. A monitoring strategy has been defined by performing sequential
580 pumping and frequent water logging in the shallower boreholes. This suggested that deep sampling
581 can be done with virtually no purge provided the borehole geometry is known and the productive
582 levels are located. Because this may not be the case, a better approach is to perform some water
583 abstraction to renew the water at the productive level(s) before doing deep sampling.

584 Complementary investigations such as video inspection and water logging give a better constraining
585 of the sampling actions.

586 This strategy has been applied to selected deep boreholes. Albeit they were not all characterized in
587 the same way, investigations have demonstrated that:

- 588 - Good reproducibility can be obtained by deep sampling when water flow is not too low, even
589 without a purging step;
- 590 - In low-yield boreholes, some preliminary water abstraction may be required in view of
591 getting samples that are more representative. An alternative approach is to have a purge-like
592 phase with several uses of the deep sampling system prior getting samples for subsequent
593 laboratory analyses;
- 594 - If the water is sampled from the cased section, or correlatively if the purging phase (not
595 associated with deep sampling) is not sufficiently developed to produce renewed water at
596 the surface, then the characterization of the aquifer chemistry can be biased: loss or gain of
597 elements or shift in isotope signatures;

598 The recommended approach to use for deep borehole characterization is to abstract a volume of
599 water equivalent to that of the screened interval or, if unrealistic, to activate/enhance water
600 circulation in the screened interval by abstracting several hundreds of liters of water. Some water
601 will be produced by the productive levels, even the low-yield ones, and appropriate deepening of the
602 sampling system in these levels will allow getting representative samples.

603

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758 Groundwater sampling in boreholes has been carried out for decades according to well-established
759 protocols and regulations. An important requirement in this context is the need to purge the
760 borehole prior to any sampling action, the volume of the purge being adapted to the water flow and
761 the regulatory context. Contaminated site investigations have introduced the concept of water
762 column heterogeneity in the screened section of boreholes, which also occurs in some
763 uncontaminated boreholes or in long-screened boreholes. Specific guidelines and practices were
764 thus introduced, in particular the concept of discrete sampling. This type of sampling can be
765 advantageously used in deep boreholes, provided that there is some renewal of water at the screens
766 or the perforated intervals. The present study aims to take a step forward in the characterization of
767 deep boreholes set up in the Aquitaine basin in France, by defining a protocol for relatively short
768 boreholes (depth < 170 m) and applying it to much deeper boreholes, formerly drilled for oil and gas
769 exploration (sampling up to 1035 m deep). Acquisitions were performed to better characterize water
770 chemistry, including some isotope considerations. They were based on physico-chemical logging and
771 endoscopic inspections where technically possible. After a review of the information provided by the
772 investigations on the characterization of the Paleocene – Eocene aquifer in southwestern France, a
773 methodology is proposed to make sampling in deep boreholes with low-yield more reliable, by
774 combining the abstraction of a reduced water volume and the use of a downhole sampling system.

775

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 777 Visualization; Funding acquisition

778 J. Barrière: Conceptualization; Writing - Review & Editing; Supervision

779 L. André: Conceptualization; Writing - Review & Editing; Software

780 A. Wuilleumier: Conceptualization; Writing - Review & Editing; Project administration; Funding
 781 acquisition; Supervision

782

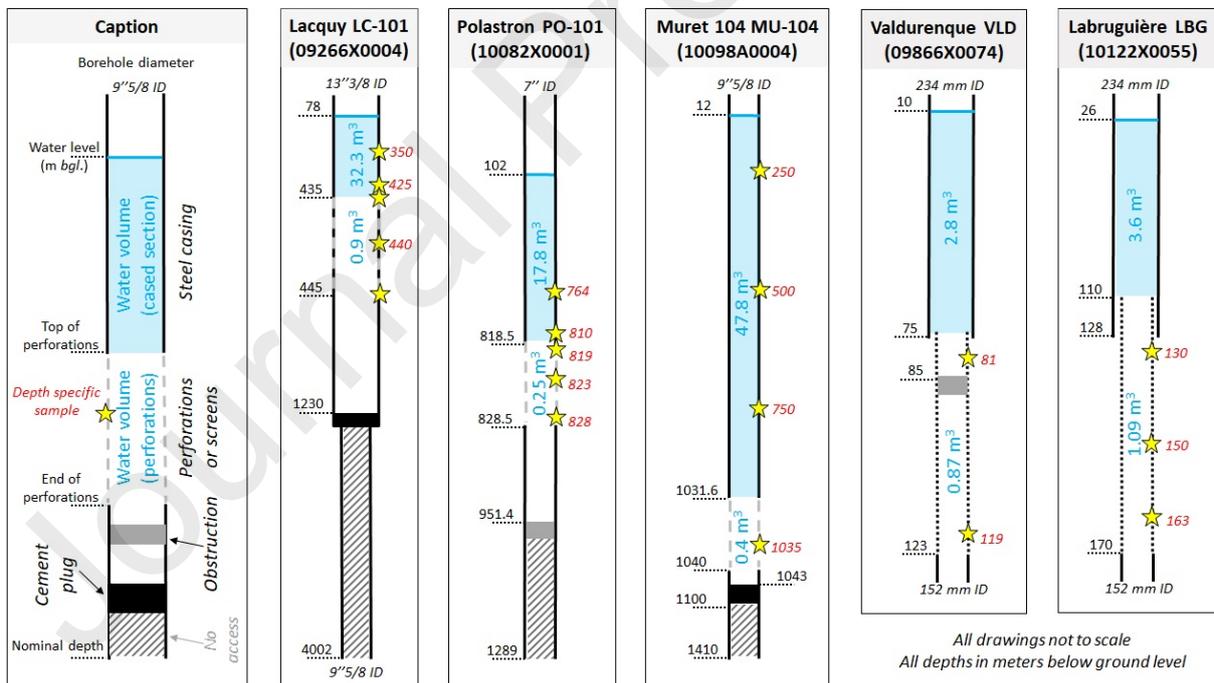
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784 **Highlights:**

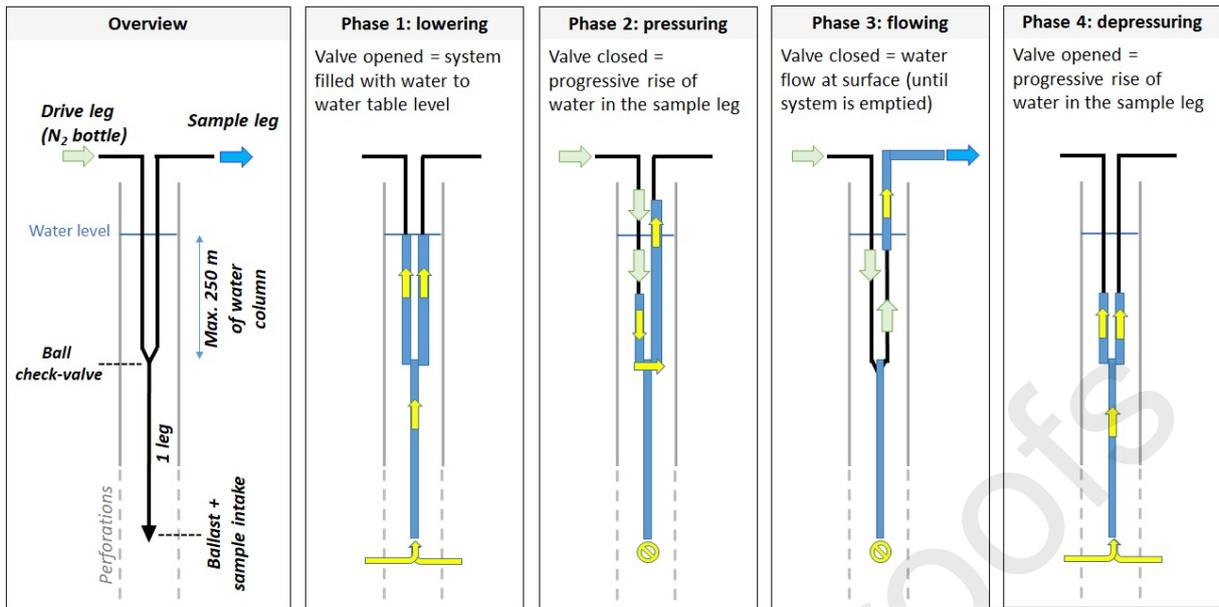
- 785 - Obtaining representative samples in deep aquifers of low-yield
- 786 - Discrete sampling at great depth using a ball check-valve operated system
- 787 - Proposition of a methodology to increase representativeness of deep sampling

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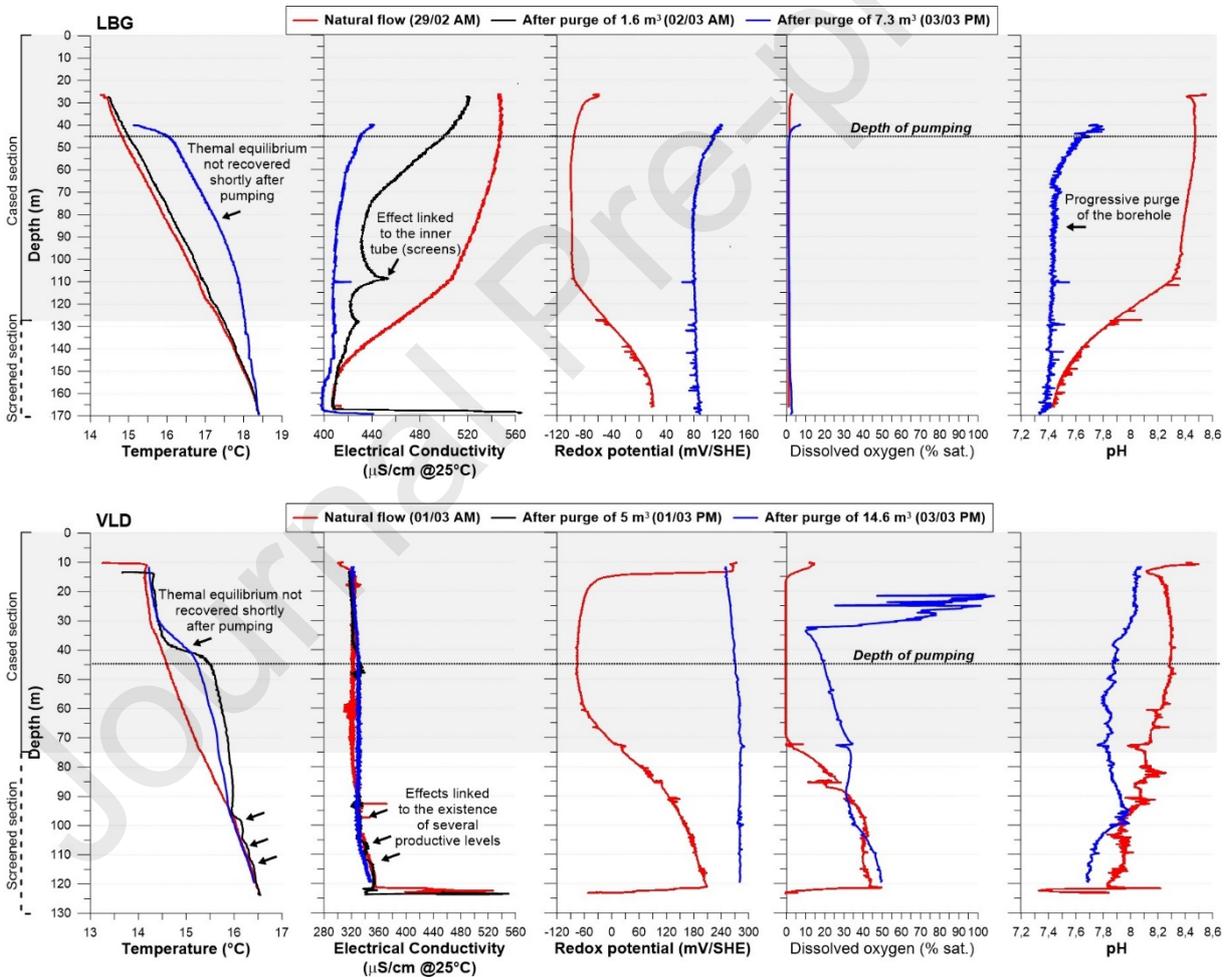
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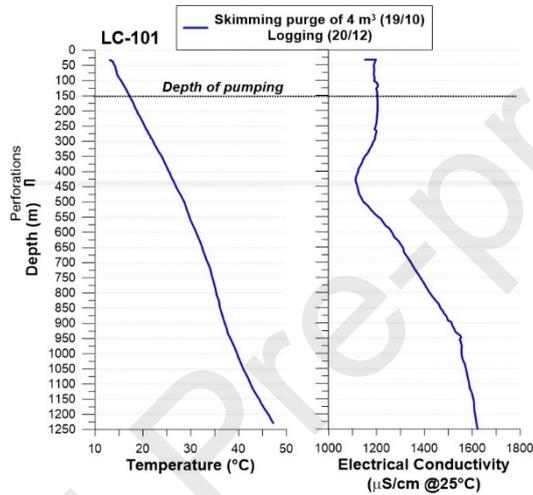
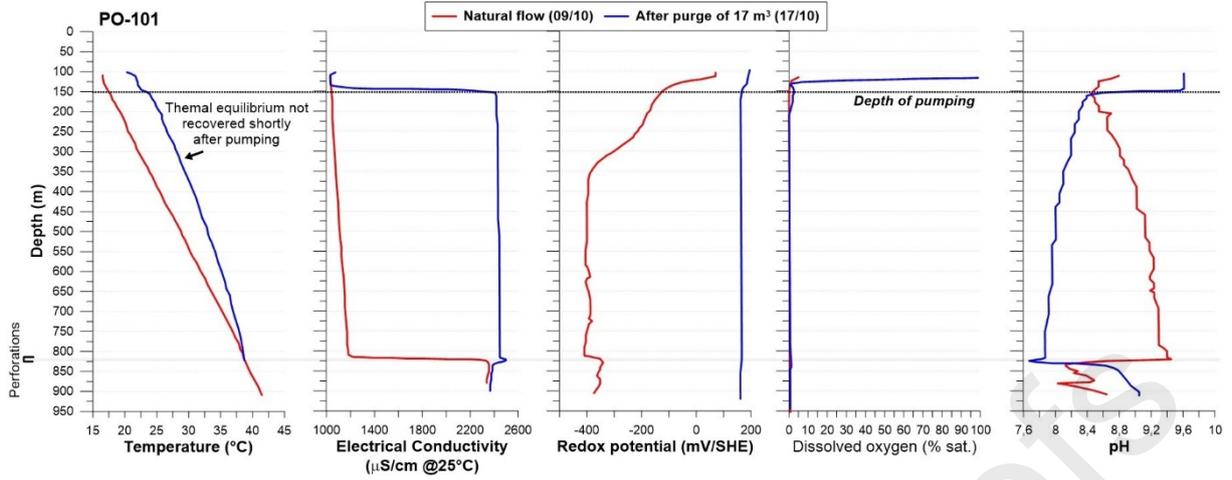
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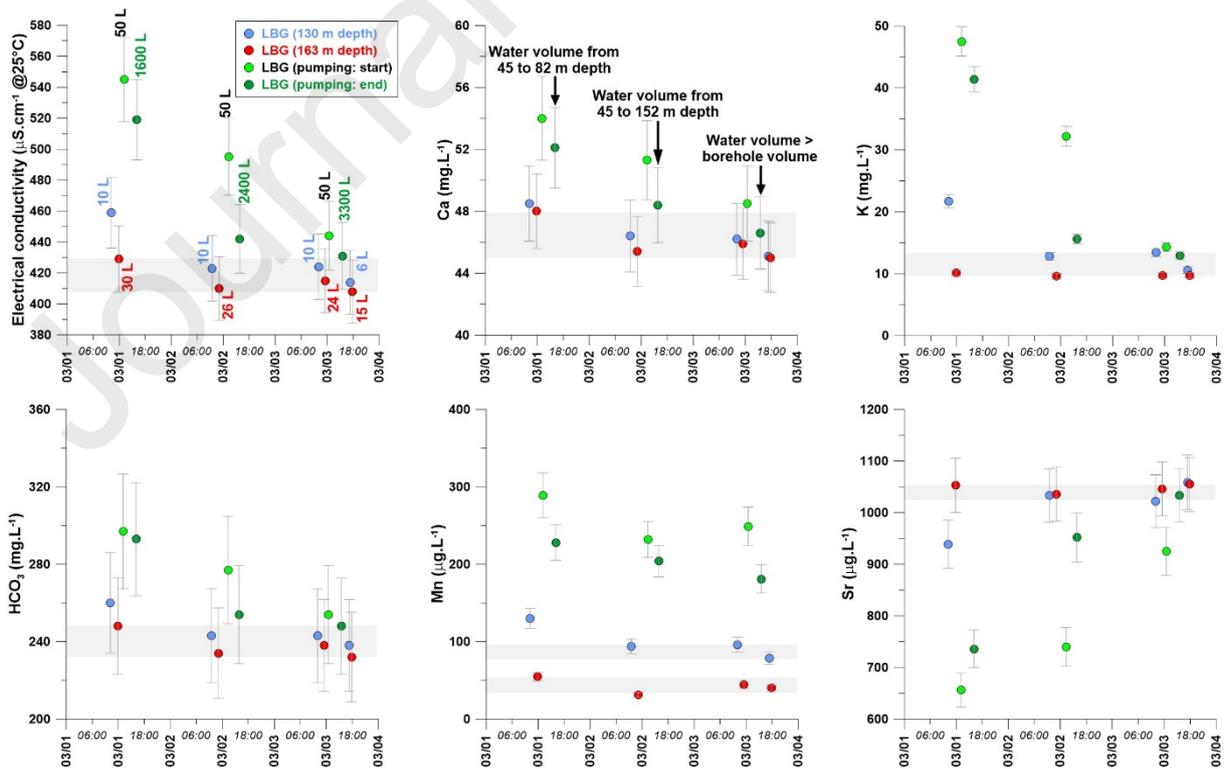
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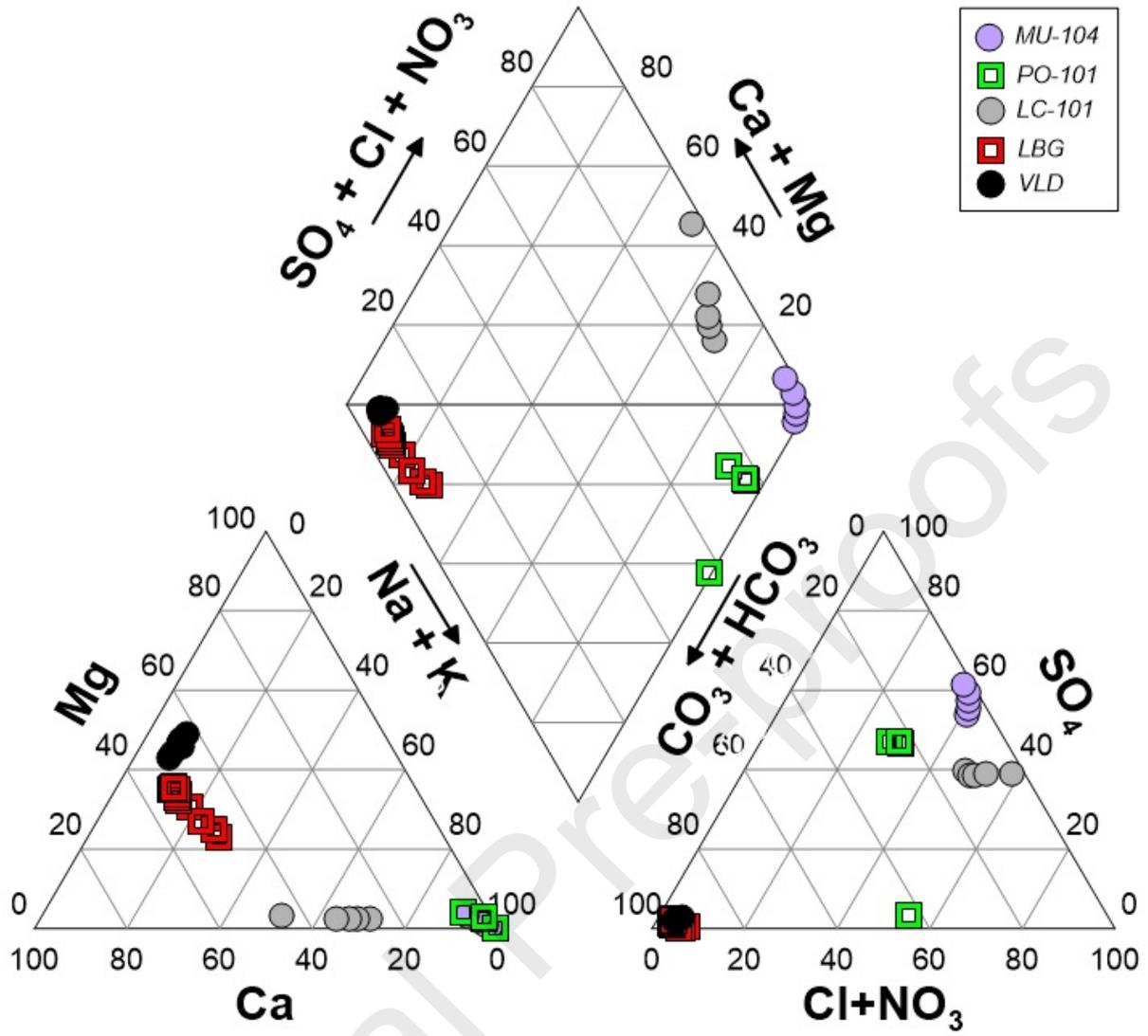
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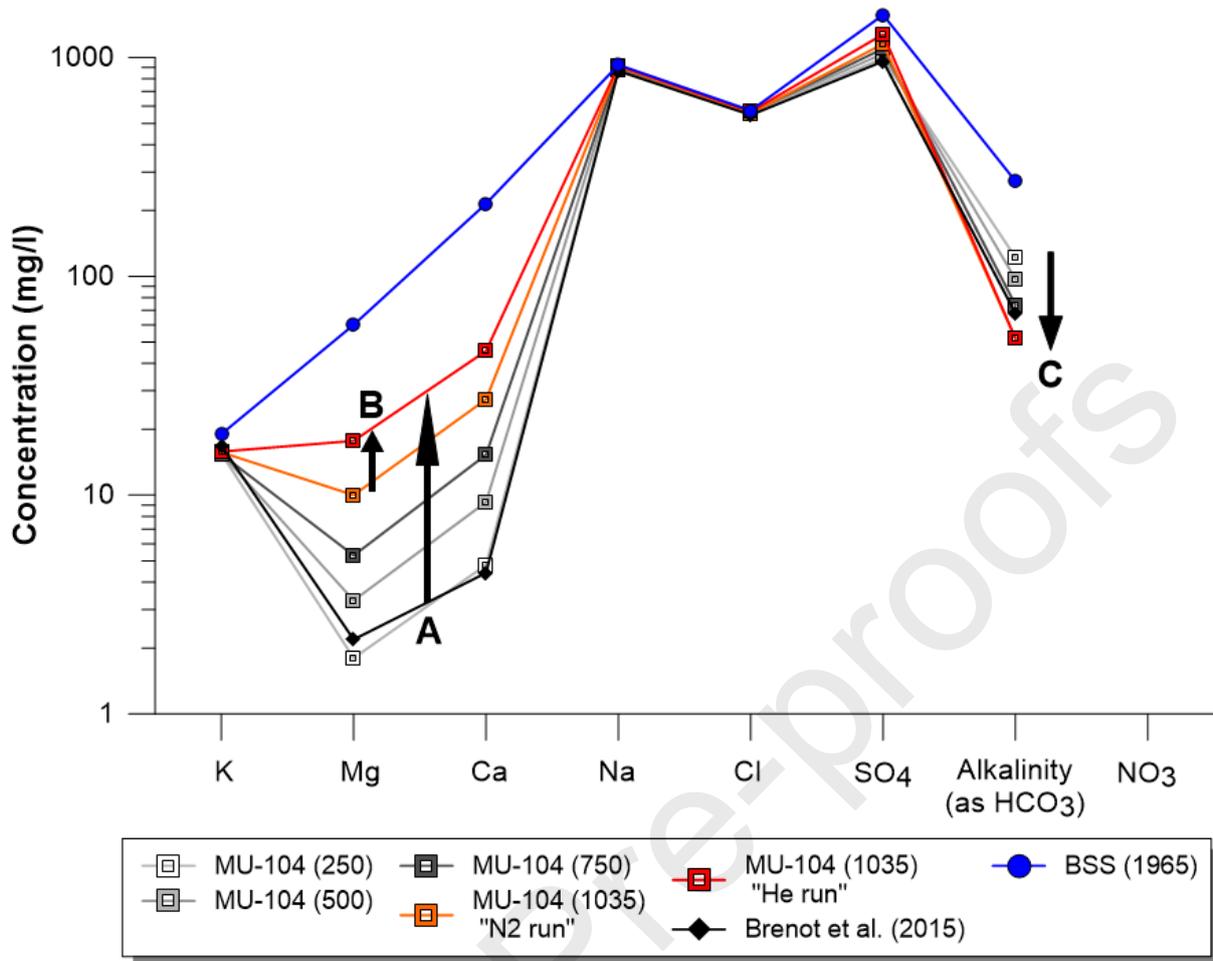
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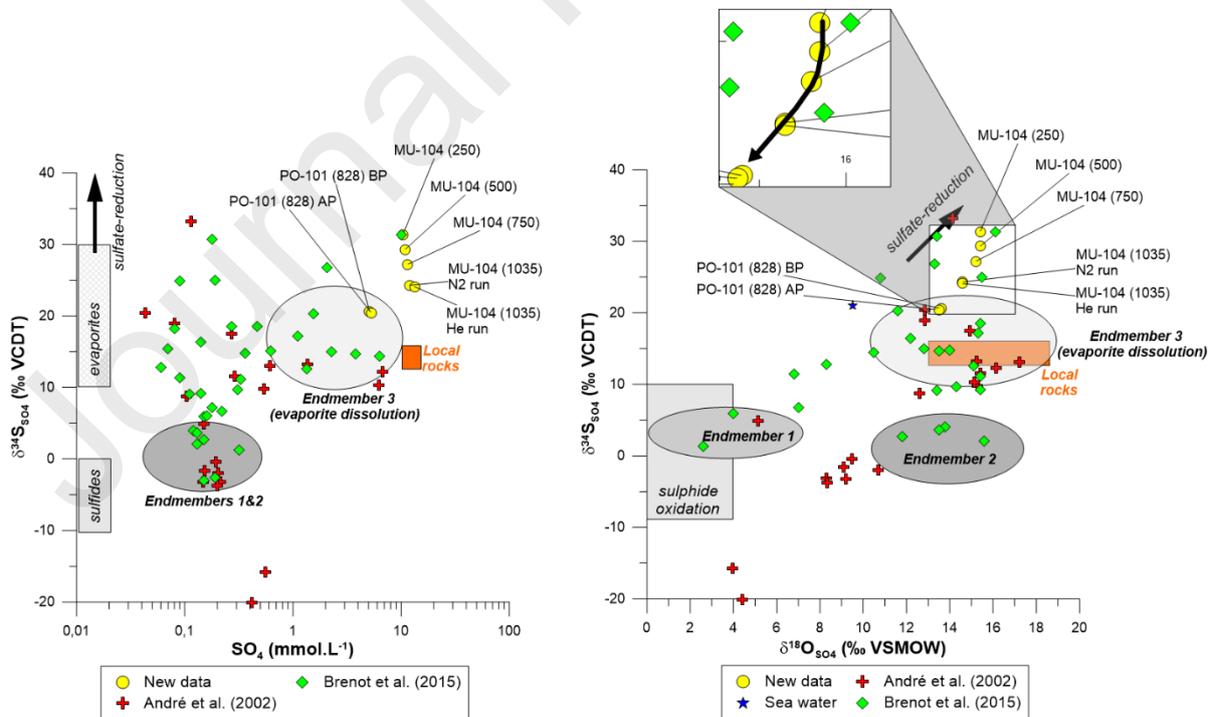
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